

THE BEHAVIOR OF BORON IN SOILS

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By FRANK M. EATON, formerly *physiologist*,² and L. V. WILCOX, *associate agronomist, Division of Irrigation Agriculture, Bureau of Plant Industry*

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INTRODUCTION

UNIVERSAL DISTRIBUTION OF BORON IN SOILS

Although boron is rarely found to occur naturally in soils in sufficient quantity to injure even sensitive plants, it is believed to be present in some concentration in all soils. This conclusion follows from evidence of two kinds. (1) Boron has always been found in plant material when appropriate analytical methods have been employed. (2) In the analysis of many hundreds of water samples from streams and wells (12, 31)³ it has been possible in each instance to demonstrate that boron was present, but sometimes there has been as little as 0.01 part per million or less.

The response that Agulhon (1), 1910, obtained from additions of boron in his experiments with crop plants grown both with nutrient solutions and with soils caused him to believe that this element had a

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³ Italic numbers in parentheses refer to Literature Cited, p. 56.

place as a fertilizer in practical agriculture. Agulhon's work and the investigations by Mazé (22) in 1914, Warrington (35) in 1923, Sommer and Lipman (33) in 1926, and subsequently by many others, provide the background for the present-day interest in the boron requirements of plants. Important diseases, such as heart rot and dry rot of sugar beets, top rot of tobacco, brown heart of turnips, cracked stem of celery, drought spot and corky core or internal cork of apples, are now known to be caused by insufficient amounts of available boron. The discoveries of the cause of the diseases just mentioned all date since 1930. The present indications point to the conclusion that many soils, while not sufficiently low in boron to bring about prominent growth abnormalities (11), may release boron to plants so slowly that greater yields would result if additional amounts were supplied.

In the western United States, as well as elsewhere in arid regions, boron frequently occurs as a constituent of irrigation waters in concentrations sufficiently high to injure cultivated crops. Instances of boron injury to plants growing on unirrigated soils are exceptional. About 1919 F. B. Headley, as a result of analyses of soils and of irrigation and ground waters, established that boron was a factor in the agriculture of the Fallon, Nev., area but no published statement of his findings was made. Shortly thereafter symptoms of plant injury were observed in several localities in the San Joaquin Valley of California that were thought to resemble those that had resulted in the Eastern States from the use of potash fertilizers carrying excessive quantities of boron as an impurity. In 1924 W. R. Schoonever associated the poor condition of a group of orange trees at Pomona, Calif., with the borax in wash waters that drained into the orchard from a packing house. This injury was brought to the attention of W. P. Kelley, who recognized the symptoms as being the same as those observed in a number of southern California localities. By the investigations of Kelley and Brown (18) it was shown that the soils of affected citrus orchards in Ventura County and elsewhere were high in water-soluble boron, that much boron had accumulated in the leaves, and, further, that in each of the larger areas examined the boron contamination was traceable to the irrigation water.

Concentrations of boron in soil solutions of greatest agricultural significance can be classified roughly as belonging in one or the other of three categories: (1) Those that are insufficient to support normal plant growth, usually below 0.1 to 0.5 p. p. m. (parts per million), (2) those that cause injury, usually in excess of 0.5 to 5.0 p. p. m., and (3) the intermediate concentrations that produce normal plant growth. Plant species exhibit wide differences both in their boron requirements and in their boron tolerances. With some plants notable injury results when the concentrations of boron best suited to growth are only slightly exceeded, whereas with others there is little change in the growth rate over rather broad ranges of concentrations.

The soils used for the work reported in this bulletin have for the most part been irrigated ones containing enough boron to permit of chemical study. Many of these soils were not sufficiently high in boron to cause injury even to sensitive crops.

GENERAL CHARACTER OF THE PROBLEM

Some of the reactions of boron with soils resemble, superficially at least, those of phosphate and arsenic. The illustrations presented in table 1 will help make this point clear. When boron is applied to the

soil in an irrigation water or is added in the form of a soluble compound such as borax or boric acid, either intentionally or as an impurity in fertilizers, a part of it remains in the soil solution and a part of it is removed from solution in forms that are not very soluble. The data to be dealt with in this bulletin show that the proportion of the boron applied that is fixed by a soil is conditioned by a number of factors, many of which are complex. Since a part of the boron applied to land is removed at least temporarily from solution, difficulties are unavoidable as regards the interpretation of toxic concentrations of boron in irrigation waters or the quantities of boron that must be applied to land if crop needs are to be fully satisfied without causing injury from excess.

TABLE 1.—*Similarity in the accumulation by soils of boron applied in irrigation waters, phosphate applied as a fertilizer, and arsenate applied as a spray to apple trees*

Depth (inches)	B ₂ O ₃ ¹ aqueous extracts, soils irrigated for—		PO ₄ (6) aqueous ex- tracts, soils fertilized for—		As ₂ O ₃ (34) 0.1 N NH ₄ Ac extract	
	3 years	40 years	6 years	15 years	Field 1	Field 2
	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
0-6.....	4.04	3.88	16.2	36.2	3.7	7.0
6-12.....		3.88	4.2	44.2	1.2	2.5
12-24.....	3.00	4.43	1.3	27.9	1.0	.6
24-36.....		3.82	.9	32.0	.7	1.3
36-48.....		3.56			.8	.4
48-60.....	2.25	3.66				

¹ Elsewhere in this bulletin boron is customarily reported as parts per million of the element. Irrespective of a general uncertainty with respect to the composition of boron compounds in soils, it is at least known that it does not occur as the sesquioxide, in which form boron is sometimes reported.

It has seemed most probable that much of the total boron of soils occurs in the form of borosilicates and other resistant boron minerals that have been transported and laid down during soil formation. Important questions exist in regard to the availability to plants of the boron represented in these diverse forms. Microscopic fragments of material such as tourmaline may hold their crystalline form and be recognized as such after many years of soil weathering (15). In addition to the described and recognizable borate minerals (29), many of which are not as refractory as tourmaline, boron often occurs in the soil as an important impurity in other relatively insoluble minerals.

Goldschmidt and Peters (17) have recently provided boron analyses of an extensive series of rocks and minerals. They used a copper electrode for their spectographic analyses, reporting that they were able to recognize boron concentrations as low as 0.0005 percent of B₂O₃, or approximately 2 p. p. m. of boron. Noteworthy, perhaps, was their finding of 300 p. p. m. of boron in a number of samples of argillaceous sedimentary rocks, a concentration 100 times as great as that found by them in German granites and gabbros and in limestones, dolomites, and biotite. Three German soils contained from 2 to 30 p. p. m. of boron. Boron was just detectable or absent, within the sensitivity of their method, in samples of obsidian and siliceous sinter, Helgoland upper chalk, and in hornblende and augite from volcanic rocks.

The aforementioned investigators were of the opinion that the boron they found in sedimentary rocks was of marine origin, which in turn they believed reflected either a primordial atmosphere high in boron or the result of boron subsequently thrown into the air by many volcanic eruptions during the course of geological time. This viewpoint is not without interest, for the sea does contain much boron. Recent determinations of the concentration of boron in the Pacific (25) and in the North Atlantic Ocean (28) show averages of 4.50 and 4.75 p. p. m., respectively. Formations that are not, at least recently, marine may yield much boron. Natural waters, for example, draining into the San Joaquin Valley from the coastal ranges of California nearly always contain appreciable concentrations of boron (12), and one stream carried as much as 15 p. p. m. Toward the top of the series of tertiary formations of the easternmost of the coastal ranges that border the San Joaquin Valley on the west arc beds regarded as clearly representative of fresh-water deposition. The waters draining from these mountains, which are practically free of granitic and similar rocks but with soft serpentines, shales, and sandstones, carry in solution not only substantial concentrations of boron but also of calcium, magnesium, and sulfate. In contrast, the waters of the San Joaquin River, which rises in the high sierra along the opposite side of the valley, may contain, even in late summer, less than 0.1 p. p. m. of boron and less than 40 p. p. m. of total solids. This water finds its source in granites and metamorphic sedimentary and igneous masses of pre-Cretaceous age. Marine soils, as judged by the quality of water they yield, may be notably low in boron. The ground waters in the marine sands and sandy shales of the Pliocene in the area immediately east of San Diego Bay, Calif., are usually somewhat saline, and yet in no instance has more than 0.33 p. p. m. of boron been found in them. One-to-five extracts of salt incrustations from the faces of recently exposed marine upper Miocene sandstone in the Tehachapi Mountains of California contained but 0.03 p. p. m. of boron in the presence of 90 mg. equivalents per liter of calcium and magnesium sulfate. Boron of magmatic origin is currently brought to the surface of the earth by waters of hot springs, which in California characteristically carry in excess of 1 p. p. m. of boron, but in our own experience there have been many exceptions.

A discussion of the occurrence of boron cannot properly be considered apart from the statement by Mellor (23, pp. 3-7), which is based on some 140 citations to the literature. Traces of boron are reported in feldspar, pegmatite, Italian limestone, travertine, basalt, sandstone, Chilean nitrate deposits, commercial caustic alkalies, iron ores (Lake Superior), aluminosilicate minerals, etc. Free boric acid has been found in the craters of extinct volcanoes, as well as in the fumaroles in Tuscany. Some relationship between the occurrence of boric acid and ammonium salts is suggested by Mellor on the basis of their having been found together in diverse cases, but the idea of an origin by the action of steam on boron nitride is discredited by him because this compound has not been found as a mineral. The boron in hot springs has been suggested as being the result of the action of steam or steam and carbon dioxide on boriferous serpentine and on tourmaline. The Strassfurt borates are pointed to as essentially magnesian, whereas in the Chilean and Californian deposits calcium predominates. Arid regions containing sodium nitrate occur near the borate deposits of

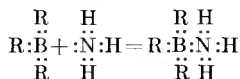
southern California, and ulexite occurs near the niter deposits of Tarapaca and Atacama, South America. The absence of magnesium from the Nova Scotia deposits is regarded by Mellor as casting doubt on their supposed marine origin.

BORON CHEMISTRY

BORON COMPOUNDS AND MINERALS

Boron, the first member of the third periodic group, is a nonmetal, being the only element with three or less valency electrons which cannot form a simple cation. Boron shows no sign of ionization, whereas aluminum, the second member of the third period, forms the trivalent cation Al^{+++} . The great affinity of boron for oxygen is shown by the ready decomposition of its hydrides in water. The halides of boron (BF_3 , BCl_3 , etc.) are volatile nonconductors which hydrolyze in water to form the stable H_3BO_3 . Boric acid is remarkable for its extreme weakness, its first dissociation constant being 1.7×10^{-9} . The ortho acid H_3BO_3 upon heating loses water to form first the meta acid HBO_2 and then the tetraboric acid $\text{H}_2\text{B}_4\text{O}_7$. The complex acid anhydrides BPO_4 and BASO_4 are reported to have the same structure, which is related to that of SiO_2 , P (or As) and B being surrounded tetrahedrally by O, each O belonging to two tetrahedra. Mellor regards these compounds as evidence of the somewhat basic nature of boron.

Trimethyl boron $(\text{CH}_3)_3\text{B}$, like BF_3 , and BCl_3 , reacts with ammonia:



In this electronic formula for R_3B , boron lends one electron to each R group (or halogen) and borrows one from each. By the coordinate linkage with ammonia, whereby the latter contributes and shares two electrons, a shell of eight outer electrons around the boron atom is completed.

The ester trimethyl borate $(\text{CH}_3)_3\text{BO}_3$, and likewise the compounds that result when mannitol or other polyhydric alcohols are added to boric acid solutions, do not give satisfactory boron color reactions in the turmeric method used for semiquantitative tests. This fact indicates that these organic boron compounds are highly stable.

It was recognized many years ago that boron trioxide or boric anhydride enters into the composition of numerous minerals, in the majority of cases in small quantities as an isomorphous admixture, replacing not acids but bases, and most frequently alumina (Al_2O_3), the amount of alumina as a rule decreasing as that of boric anhydride increases. This substitution is explained by the similarity between the atomic composition of the oxides of aluminum and boron. Sodium, potassium, calcium, or magnesium borosilicates find their counterparts in aluminosilicates.

Singer (32) prepared in the laboratory, by the fusion of SiO_2 , Na_2O , $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and other oxides, an extensive series of zeolites such as $\text{NaKO} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 4\text{H}_2\text{O}$, $\text{Na}_2\text{O} \cdot 0.5\text{B}_2\text{O}_3 \cdot 0.5\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 4\text{H}_2\text{O}$, $\text{Na}_2\text{O} \cdot 0.5\text{B}_2\text{O}_3 \cdot 0.5\text{Mn}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 4\text{H}_2\text{O}$, $\text{Na}_2\text{O} \cdot 0.5\text{B}_2\text{O}_3 \cdot 0.5\text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 4\text{H}_2\text{O}$. By these he showed that Al_2O_3 could be replaced (in manufacture) by equivalent amounts of B_2O_3 , V_2O_3 , Mn_2O_3 , Fe_2O_3 , and Co_2O_3 . These latter zeolites did not possess as

high a sodium-calcium exchange capacity as the Al_2O_3 zeolites represented by the first example, the sodium-to-calcium exchange capacities of the above series of zeolites being respectively 98.0, 8.1, 13.9, 10.2, and 9.4 percent.

Sodium tetraborate is a relatively soluble salt, and boric acid has a solubility in water of about 5 percent at 20°C . Calcium borate at 30° has a solubility of 0.31 percent, which is about 50 percent greater than the solubility of calcium sulfate. Among some of the simpler of the naturally occurring borate minerals that are easily brought into solution in water there may be mentioned borax, $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$; kernite, $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$; colemanite, $2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$; and ulexite, $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$. Schaller (29) lists and gives the composition of "all the known boron minerals" as of 1929. There are 56

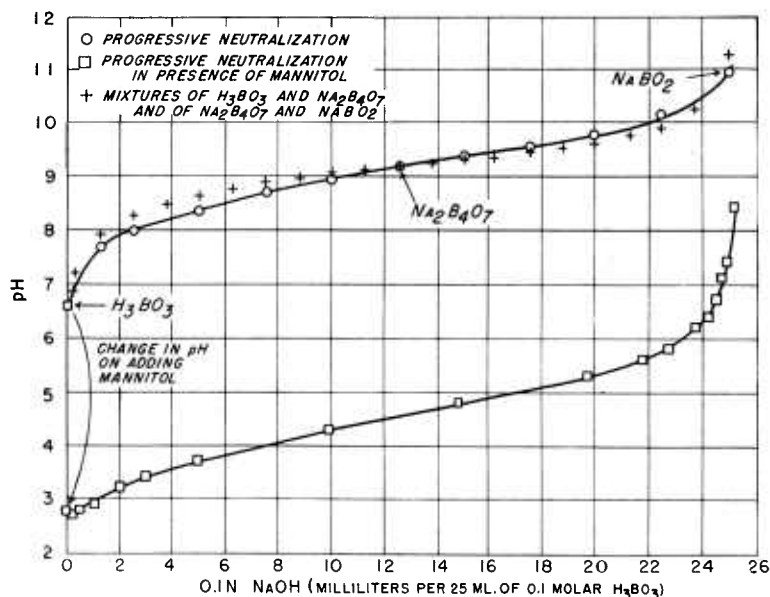


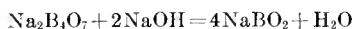
FIGURE 1.—Titration of boric acid with sodium hydroxide in pure solution and in the presence of mannitol.

entries. Nine are classified as containing no water and no silica, which series includes borates with iron, magnesium, manganese, and other bases in varying proportions, as well as a simple aluminoborate, $\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$. Twenty-seven have water and no silica, in which series calcium and magnesium borates, with varying amounts of water, are prominent. With or without these bases, iron and tin, as well as sodium and potassium, occur, and also a calcium boroarsenate and a magnesium borophosphate. None of these hydrous minerals without silicon contain aluminum. Of the 20 minerals with silica, about half contain aluminum as well. Many of the borosilicates are highly resistant to weathering.

REACTIONS OF BORIC ACID AND SODIUM BORATE

A 0.1 molar aqueous solution of pure boric acid has a pH value of about 6.6 (fig. 1), whereas a solution of hydrochloric acid of equal

molar concentration has a pH value of about 1.0, representing a 400,000-fold difference in the concentration of active hydrogen ion. The fact that boric acid is an extremely weak acid makes it impracticable to titrate it with sodium hydroxide in the presence of a color indicator. The equivalence point is highly alkaline, having a pH value of about 11.0, and the "break" ordinarily associated with the end point of an alkali-acid titration is so slight as to be hardly perceptible. The titration can be conducted with electrometric equipment such as hydrogen or glass electrodes. The following equations represent the reactions:



Under these conditions boric acid acts as a monobasic acid. At the point of half neutralization the composition corresponds to $\text{Na}_2\text{B}_4\text{O}_7$ or borax, which in 0.1 normal concentration has a pH value of 9.2. At the end point sodium metaborate is formed, NaBO_2 , and, as indicated in figure 1, the pH value is about 11.0.

In order to determine boric acid volumetrically, use is made of a reaction involving some one of several polyhydric alcohols, notably glycerol or mannitol. Upon the addition of mannitol, for instance, to an aqueous boric acid solution, one H^+ is liberated for each molecule of boric acid present. This can be titrated with sodium hydroxide, using phenolphthalein as indicator. This acid complex is similar in activity to acetic acid; in fact, a titration curve of the latter can be superimposed with rather close fit on the mannitol-boric acid curve of figure 1. The reaction between a polyhydric alcohol and boric acid forms the basis for practically all volumetric methods for the quantitative determination of boron. A qualitative and semi-quantitative method, depending on the color reaction of curcumin (a constituent of turmeric root extract), has been used to some extent.

The H_3BO_3 - NaBO_2 graphs (fig. 1) were derived by two distinct procedures, but the results were substantially the same. The points marked with crosses were obtained by mixing 0.1-normal solutions of boric acid and sodium tetraborate and of sodium tetraborate and sodium metaborate in proportions to give the sodium concentrations shown. The second series of measurements, marked by circles, which have been traced, was obtained by the progressive neutralization of boric acid with sodium hydroxide. A hydrogen electrode was used in the first series and a glass electrode in the second. In both series each point represents a separate solution that was made to volume before the pH determination in order to eliminate any dilution effect.

ANALYTICAL METHODS

During the course of this investigation boron has been determined by direct electrometric titration (2, pp. 30-33; 37) in the presence of mannitol when present in solutions with no more than a trace of phosphate and only small amounts of iron, aluminum, or silica. When interfering substances have been present that could not be removed by lead nitrate clarification, the titrations, either electrometric or colorimetric, have been preceded by methyl alcohol distillation (36) of the boron.

FIXATION OF BORON BY SOILS

THEORETICAL CONSIDERATIONS

The subject of boron fixation by soils and the related one—the solubility of soil boron—will be dealt with under a number of subsequent headings. As a part of the background for the investigation, the observation had been made (12, pp. 19–20) that when a series of 10 irrigated soils were repeatedly leached with distilled water, measurable concentrations of boron were released through the twentieth leaching. The behavior of the boron held by these soils was thus at variance with behavior of chloride and sulphate, very little of either of the latter having been found in the third or subsequent percolates. The adsorption characteristics, or the forms in which boron was held, were thus indicated as meriting further study. It had also been found that heavy applications of irrigation water in basins thrown up around trees in boron-injured lemon orchards did not change the concentration of boron found in 1-to-5 extracts of the soil, notwithstanding marked reductions in the concentrations of other solutes. These and other observations pointed to the fixation of boron by soils and to tendencies toward the maintenance of equilibria with soil solutions.

Three general mechanisms for the fixation of boron added to soils are recognized as meriting consideration. Ideas concerning these mechanisms—ionic exchange, molecular adsorption, and chemical precipitation—are inclined, however, to run together somewhat when one undertakes to press definitions too closely. Though substantial reasons may exist for differentiating between these principles, it does not follow that statements can be made under any given circumstance as to which one, to the exclusion of the others, has been operative.

The possibility of boron fixation by the substitution of negatively charged borate ions for the OH ions, which are so prominent on the surface and within the crystal lattice of freshly ground minerals, has been regarded as one of the more promising bases for causal mechanism explorations. In the process of rock weathering and soil development all exposed OH ions would have been repeatedly subject to replacement by other anions of the soil solution. The fixation of boron by anion exchange accordingly raises important questions not only of anion exchange capacities but also of concentrations and of the exchange energies of the previously absorbed anions relative to boron. There are also involved considerations bearing on the question of the exchangeability of boron for the silicon of the clay minerals as well as of the relationships between boron and aluminum, both of which are amphoteric elements of the third periodic group.

Molecular adsorption—usually illustrated by the fixation of gases on solid surfaces, the removal of coloring matter and weak electrolytes from solution by charcoal, and the adsorptions of moisture by colloidal and other materials—may or may not be operative in the fixation of boron compounds. As is shown later in this bulletin, boron is fixed by a material such as magnetite at a pH value such that boron would exist almost wholly as boric acid.

RELATION OF SOIL-SOLUTION CONCENTRATIONS TO FIXATION

Much advantage is gained in fixation studies if the initial material is free of the constituent to which attention is directed. In the instance of boron in soils this has not been possible. All soils can be

expected to yield at least a little boron when suspended in water. Likewise, in all tests, boron has been observed to be absorbed by the soil if the solution concentration is made sufficiently high. Conditions such as temperature, acidity, and time will be dealt with as among those that influence fixation and solubility.

The series of measurements reported in table 2 were undertaken with practical as well as general investigational objectives. The soils used were collected in San Fernando Valley, Calif., where, since about 1916, water from the Owens Valley has been extensively used. This water supply, during the period of observation since 1928, has had an average of about 0.65 p. p. m. of boron, and as a consequence many of the lemon plantings have developed a substantial degree of boron injury. In many cases the injury is severe, but some orchards, on the other hand, have shown relatively few symptoms. Among the factors apparently influencing the severity of injury there has been evidence of a relationship with soil type, but this has not always been clearly defined.

Effort was made to find locations in or adjacent to the selected orchards where irrigation water and hence boron had not been applied. In this effort the writers apparently were not very successful, inasmuch as the distilled water extracts from three of the four soils contained higher concentrations of boron than are customarily found in unirrigated soils, but less boron than has been found in the soil solutions of the regularly irrigated portions of these particular orchards.

It was hoped that there might be established from the measurements that were undertaken on these soils (1) something of the general magnitude of the boron-fixing power of soils, (2) whether there existed substantial differences in the boron-fixing power of different soils, and (3) whether differences in fixing power could be related to tree and soil conditions in orchards treated alike as regards the irrigation supply. The experiment was so arranged that information would be provided on the effect of drying and long standing on boron fixation.

The soils from selected orchards were weighed into mason jars in quantities of 500 or 1,000 gm. and wetted to three-quarters of their saturation percentages with solutions of boric acid adjusted in concentration to introduce the desired quantities of boron. At this moisture content enough solution for a boron analysis can be removed from a soil by the application of air pressure in a filter chamber. At a low moisture content a relatively great change is effected in the concentration of the soil solution by a little adsorption of boron. Likewise, at low moisture content, there is a minimum dilution of other constituents of the soil solution, which may or may not be reactive in boron fixation. While drying, the series of soils designated C in table 2 were placed in an oven heated by hot-water coils. The temperature of this oven varied between 40° and 50° C. Otherwise all soils were held in capped jars in a basement vault where there was little change in temperature.

TABLE 2.—*Fixation of boron by soils collected in San Fernando Valley, Calif.*¹

Soil No.	Soil classification	Moisture equivalent	Saturation percentage	Boron added	Initial solution concentration	Boron fixation under treatment indicated		
						A	B	C
		Percent		Mg. per kg.	P. p. m.	Mg. per kg.	Mg. per kg.	Mg. per kg.
241	Hanford gravelly sandy loam.....	5.3	18.2	0.0	2.0			
				.5	5.7	0.3	0.3	0.3
				1.0	9.3	.3	.6	.6
				2.0	17.0	.9	1.0	1.1
				3.0	24.0	1.2	1.2	1.7
				4.0	31.0	1.4	1.6	1.9
				6.0	46.0	1.9	2.3	3.7
				8.0	61.0	2.5	3.2	3.6
				10.0	75.0	2.5	3.2	4.6
				15.0	112.0	3.7	4.3	6.2
				20.0	149.0	3.1	5.3	8.4
				25.0	189.0	5.1	6.6	8.9
				50.0	368.0	5.2		
				100.0	735.0	13.0		
				200.0	1,467.0	16.0		
				400.0	2,932.0	21.0		
242	Hanford sandy loam.....	13.5	25.3	.0	1.1			
				.5	3.7	.4	.3	.3
				1.0	6.4	.7	.8	.7
				2.0	12.0	1.3	1.4	1.4
				3.0	17.0	1.5	2.1	2.0
				4.0	22.0	2.2	2.4	2.5
				6.0	33.0	3.3	3.5	3.5
				8.0	43.0	4.2	3.8	4.7
				10.0	54.0	5.1	5.9	5.9
				15.0	80.0	6.2	8.9	8.3
				20.0	107.0	8.3	10.0	10.5
				25.0	133.0	10.0	13.0	12.6
				50.0	265.0	17.0		
				100.0	527.0	23.0		
				200.0	1,055.0	45.0		
				400.0	2,110.0	69.0		
243	Yolo loam.....	17.1	31.8	.0	1.1			
				.5	3.2	.3	.2	.3
				1.0	5.3	.4	.6	.6
				2.0	9.5	.8	.9	1.1
				3.0	14.0	1.3	1.4	1.6
				4.0	18.0	1.8	1.7	2.0
				6.0	26.0	2.0	2.5	2.8
				8.0	35.0	2.4	2.7	3.6
				10.0	43.0	2.8	3.8	4.6
				15.0	64.0	4.6	5.2	6.5
				20.0	85.0	6.5	5.3	8.3
				25.0	106.0	5.5	6.8	9.4
				50.0	211.0	7.6		
				100.0	420.0	12.0		
				200.0	859.0	17.0		
				400.0				
244	Dublin clay loam.....	24.6	44.8	.0	.3			
				.5	1.8	.2	.3	.4
				1.0	3.3	.4	.7	.8
				2.0	6.3	1.1	1.8	1.4
				3.0	9.2	1.6	1.8	2.2
				4.0	12.0	2.3	2.3	2.6
				6.0	18.0	3.4	3.6	3.3
				8.0	24.0	3.7	4.8	5.1
				10.0	30.0	5.2	5.8	6.2
				15.0	45.0	6.7	7.7	8.6
				20.0	60.0	6.9	9.7	10.6
				25.0	75.0	10.7	12.0	8.3
				50.0	150.0	9.4		
				100.0	298.0	28.0		
				200.0	596.0	37.0		
				400.0	1,191.0	59.0		

¹ The soils were wetted to three-fourths of their respective saturation percentages with solution containing the indicated quantities of boron. At the end of the periods sufficient solution was removed from each in a pressure filter for the boron determinations. The 3 treatments were as follows: A, Soils wetted for 30 days; B, soils wetted for 300 days; C, soils rewetted for 30 days after having been wetted for 40 days and dried at 40°-50° C. for 20 days.

None of the jars were set up in duplicate, and only sufficient soil was used to yield 20 to 40 ml. of solution for analysis. As a consequence, there are occasional values that are clearly out of line because of errors attributable to small samples and the character of the procedure. This experiment was among the first in which boron determinations by direct titrations were undertaken on very small portions of soil extract. Later refinements in the technique of extraction and analysis, as well as of the method of adding water and boron solutions to soils, have permitted increased accuracy. For a given investment of time and effort, the purpose of this experiment was served better by

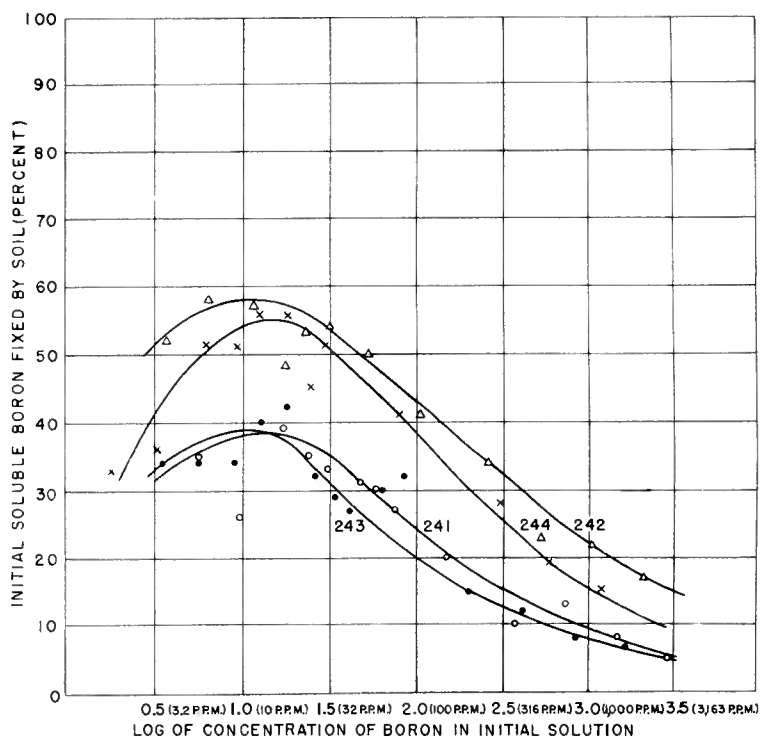


FIGURE 2.—Fixation of boron by soils wetted to three-fourths of their saturation percentages with solutions of boric acid. (Numbers refer to soil samples as in table 2.)

extensive sequences and a number of treatments than by fewer duplicate or triplicate measurements.

Within the limits of this experiment, each increment in the quantity of boron added to the soils brought about further fixation, but the proportion of the boron introduced that was fixed (fig. 2) decreased as the concentration of boron in the solution was made to exceed 10 or 15 p. p. m. It is found further that the boron in the original soils served to depress fixation of boron from solutions of low concentrations. This is necessarily so since the concentrations of boron in the solutions

of the soils to which no boron was added represent equilibrium concentrations between the boron previously fixed and that in the aqueous phase. The adsorption curves suggest that if these soils had been initially free of boron the highest percentage adsorption might have resulted from the smallest additions.

Increasing from 30 to 300 days the period during which the soils stood in contact with the boron solutions (treatments A and B respectively) increased fixation slightly in all soils. About 15 percent more of boron was fixed by soil 244 in the long period than in the short period.

Two of the four soils, 241 and 243, were found to fix substantially less boron than the other two (fig. 2). Lemon orchards grown on soils 241 and 243 under irrigation were severely injured by boron, and the boron content of the leaves (table 3) was relatively high. Soils 242 and 244 had higher fixing power, and the corresponding orchards showed less injury and there was less boron in the leaves. The results indicate that it is possible to appraise in the laboratory the general order of boron-fixing power of soils and that this appraisal can be expected to correlate with field injury. It does not follow from these results that soils such as 242 and 244 under continued irrigation would not eventually build up soil-solution concentrations as high as soils 241 and 243.

TABLE 3.—*Degree of injury and extent of boron accumulation by lemon leaves in relation to the boron-fixing power of soils*

Soil No.	Boron-fixing power of soil ¹	Leaf injury ²		Boron in leaves	
		1931	1936	1931	1936
	Percent			<i>P. p. m.</i>	<i>P. p. m.</i>
241	32	8	7	894	865
243	33	6	4	796	674
244	52	4	4	555	475
242	54	1	2	289	363

¹ Averages of treatment A for 0.5 to 10.0 mg. additions (table 2).

² Injury is graded on a scale of 1 to 10 wherein a grade of 1 is assigned when there is no burning or yellowing and a grade of 10 for the most severe injury that has been observed.

Desiccation followed by resuspension (treatment C) reduced the solubility of the boron added to these soils. The effect of drying was substantially greater in the instance of soils 241 and 243, which had low boron-fixing powers, than in the instance of soils 242 and 244, which had high boron-fixing powers. The boron fixed by soil 241 was increased upward to 50 percent by drying. By this divergence in the fixation responses of soils 241 and 243 as compared with soils 242 and 244 it is indicated that the fixation reactions that establish equilibrium under moist conditions are to be differentiated from those that accompany drying.

EFFECT OF TIME AND OF DRYING ON BORON SOLUBILITY

In this section additional data on the effects of time and desiccation on boron release and fixation are presented which confirm those of table 3. The methods were somewhat different in this series of

tests, in that 1-to-5 soil-water suspensions were employed, the proportion of water being 15 to 25 times as great in this case as in the former. Three suspensions of each of the six soils were set up. One of these was with distilled water, one was with a 5 p. p. m. boron solution, and one was with a 25 p. p. m. boron solution. Aliquots of the suspensions were withdrawn as follows: A, after standing for 30 days; B, after suspensions had stood for 3 years; C, after standing for 30 days followed by drying and resuspending for 24 hours; and D, after drying and resuspending for 30 days. The suspensions of the C and D series were dried by exposing them in open beakers in the greenhouse.

Relatively large volumes of solution were available for all boron determinations, and all of the measurements accordingly are regarded as dependable. Boric acid solutions of the same concentration as those added to the soils were held in glass jugs, and account was taken of minor changes in their concentrations in the computations of boron release and fixation. All of the soils except the first of the two Montezuma loams, No. 176, were irrigated. Soil 176 was from a grainfield immediately across a fence from a prune orchard represented by soil 179. The results are shown in table 4.

Time as represented by 30-day and 3-year periods (treatments A and B respectively) was a factor of some importance in its effect on the release of boron from the soils in the distilled-water series. The evaluation of the time effect is made a little uncertain, however, by the fact that the pH values of the suspensions increased during the period of the test. It seems evident that the progress of boron dissolution was checked and in some cases more than offset by the shift toward alkalinity.

Drying was essentially without effect on the solubility of soil boron in the distilled-water suspensions. This can be taken to mean that the permanent changes that may result from this cause had already resulted as a consequence of repeated wetting and drying in the field before the samples were collected.

The measurements, in conformity with those of the preceding section, show that drying has a definite effect on fixation when new boron is added to the soil (treatment D compared with treatment A). This effect is evident in the 5-p. p. m. series, but it is more pronounced in the 25-p. p. m. series.

These results point to the conclusion that after a soil to which boron has been added has dried out a number of times there may be little additional change in the solubility of the boron or, by inference, in the form in which it is held in the soil. When new boron is added to a soil, however, drying is an important adjunct to fixation. When soils are dried, the concentrations of all soil-solution constituents are increased to saturation, which is followed by precipitation. In the soils without added boron this precipitation is reversible, since on rewetting, the initial concentrations are again found. When boron is added to the soil and then dried, however, a part of that which has been added is not recovered on resuspension.

TABLE 4.—*Effect of time and drying on release and fixation of boron by six soils*¹BORON IN SOLUTIONS AT END OF PERIODS¹

Soil No.	Soil classification	Distilled-water series				5-p. p. m. boron series				25-p. p. m. boron series			
		A	B	C	D	A	B	C	D	A	B	C	D
1	Sierra loam	P. p. m. 0.10	P. p. m. 0.67	P. p. m. 0.14	P. p. m. 0.12	P. p. m. 4.74	P. p. m. 4.04	P. p. m. 4.06	P. p. m. 4.42	P. p. m. 24.69	P. p. m. 24.23	P. p. m. 21.77	P. p. m. 22.48
8	Yolo fine sandy loam	.20	.36	.20	.24	4.37	4.52	3.77	4.38	22.95	24.18	20.74	18.82
176	Montezuma loam	.10	.11	.08	.08	3.43	3.24	3.20	3.20	22.92	24.18	20.74	18.82
179	do.	3.05	2.96	2.27	3.20	6.75	6.38	3.96	6.60	23.72	21.89	19.46	22.08
177	Rincon loam	.50	.38	.58	.50	4.18	4.12	3.90	3.82	22.58	23.23	20.06	21.42
181	Yolo loam	.25	.33	.20	.20	4.64	4.71	3.91	4.46	23.49	23.22	20.26	22.28

BORON RELEASED (—) AND FIXED PER KILOGRAM OF SOIL (+)

Soil No.	Soil classification	Milli-grams				Milli-grams				Milli-grams				Milli-grams
		—	—	—	—	—	—	—	—	—	—	—	—	
1	Sierra loam	—0.50	—0.35	—0.70	—0.60	+1.00	+0.50	+4.40	+2.60	+3.55	+2.85	+15.15	+11.60	
8	Yolo fine sandy loam	—1.00	—1.80	—1.00	—1.20	+2.85	+2.10	+5.85	+2.80	+9.60	+3.10	+22.20	+15.90	
176	Montezuma loam	—1.50	—1.55	—1.40	—1.40	+7.55	+8.50	+8.70	+10.30	+19.90	+29.75	+35.30	+30.00	
179	do.	—15.25	—14.80	—11.35	—16.00	—9.05	—7.20	—1.10	—8.75	+5.05	+14.30	+26.20	+13.60	
177	Rincon loam	—2.50	—2.90	—2.90	—3.00	+3.80	+1.60	+4.90	+5.60	+12.20	+17.60	+23.70	+16.90	
181	Yolo loam	—1.25	—1.65	—1.00	—1.30	+1.50	+1.15	+5.15	+2.40	+6.55	+7.65	+22.70	+12.60	

MISCELLANEOUS CHARACTERISTICS OF THE SOILS USED

Soil No.	Soil classification	1-to-5 extracts				Boron			
		At end of treatment B		25-p. p. m. boron series		Displaced solution		Sum of three hot-water extracts per kilogram	
		Freshly prepared	Distilled-water series	5-p. p. m. boron series	pH	pH	pH	P. p. m.	Milligrams
1	Sierra loam	Percent 8.4	pH 7.2	pH 7.7	pH 7.5	pH 7.7	pH 7.7	0.69	0.79
8	Yolo fine sandy loam	22.3	7.5	7.9	7.9	7.8	7.8	.63	1.72
176	Montezuma loam	21.1	6.7	7.3	7.4	7.6	7.6	—	2.89
179	do.	25.3	7.3	7.9	7.9	7.7	7.7	6.61	21.26
177	Rincon loam	13.6	—	7.8	7.8	7.8	7.8	—	4.80
181	Yolo loam	15.4	6.9	7.7	7.7	—	—	.93	1.55

¹ In this experiment 500-gm. portions of soil were added to 2,500-ml. portions of distilled water and to solutions of boric acid containing 4.95 p. m. (5-p. p. m. series) and 24.80 p. m. (25-p. p. m. series) of boron. The aliquots for the various treatments were withdrawn while the soil was suspended by vigorous shaking. The treatments were as follows: A. Time, 30 days; shaken daily. B. Time, 3 years; shaken several times a year. C. After 30 days as in A, the solution was evaporated and the soil air-dried and then taken up in original volume of water for 24 hours. D. Same as in C except taken up and shaken daily for 30 days after air-drying.

RELATION OF HYDROGEN-ION CONCENTRATION TO SOLUBILITY OF BORON IN SOILS

Soil acidity and alkalinity have been looked upon throughout the investigations here reported as having an important influence on the fixation and availability of boron in soils. Early tests, for example, showed that soil suspensions brought to pH values between 3 and 4 by the addition of hydrochloric acid yielded higher concentrations of boron upon extraction than did suspensions made up by the addition of water alone. No systematic measurements over a range of hydrogen-ion concentrations were made, however, until much of the work reported elsewhere in this bulletin had been completed.

For the purposes of the study, a series of acid and alkaline 1-to-1 suspensions were prepared of stock soils 2, 5, and 10 and of soil 293. Preliminary trials were made to determine the quantities of hydrochloric acid and sodium hydroxide required to establish the desired ranges in pH values. The original pH ranges of soils 2, 5, and 10 were extended by subsequent series, but the supply of soil 293 was not sufficient to permit its use in these extensions. The several suspensions comprising each series were allowed to stand for 48 hours or longer with recurrent shaking before filtration. The pH measurements and boron determinations were made on the filtered extracts of the 1-to-1 suspensions. Boron was not added to any of the soils in the laboratory, but all were from fields that had been irrigated for 10 years or longer. Other than for the fact that the soils used were known to yield substantial quantities of boron upon extraction with water, none were selected because of known peculiarities or special characteristics. In other words, they were merely four soils containing enough water-soluble boron to make them suitable for the investigation.

Soil 10 proved to be highly buffered above pH 9, and relatively large amounts of sodium hydroxide did not cause the suspensions to become strongly alkaline. Filtration became progressively more difficult as sodium hydroxide was added. The calcium carbonate content of soil 2 was especially high, and the quantity of acid required to shift the pH value to the lower levels was substantial. The points of soil 2 do not align themselves to form a smooth curve as do the points of soil 10, which were notably regular (fig. 3). As to this poor alinement of the points along the curve for soil 2, it can only be suggested that boron equilibrium between the solid and solution phases was incomplete at the end of the 48-hour period, making noticeable the effects of small variations in time. (See table 14 in this connection.) At the highest hydrogen-ion concentration much iron, and possibly aluminum, came into solution from soil 2, interfering with the direct titration of boron and making it necessary to resort to the distillation method for the determination. The boron concentration at pH 5 for soil 293 is regarded as being significantly lower than that found at the next higher pH value. Although there was not enough soil for a repetition or extension of the measurements of soil 293, some confirmation was obtained by rewetting and reextracting the whole series of 293 soils after they had stood for 48 hours. The new series of points closely paralleled those shown, but the boron concentrations were somewhat lower.

In one respect, each of these four soils (fig. 3) responded similarly to changes in hydrogen-ion concentrations, in that between pH 9.0

and pH 5.5 the concentration of boron in the solutions increased from twofold to fivefold. In respect to the character of the extensions of the curves beyond these pH values there is a marked distinction between the soils. The responses of soils 2 and 5 are quite different from the responses of soils 10 and 293. The apexes of curves 2 and 5 are at points of lowest boron solubility, whereas the apexes of curves 293 and 10 are at points of highest boron solubility. An explanation of this evidently significant difference in behavior is not afforded by the data at hand. Neither is it known which, if either, of these two types of reactions are more representative of soils generally.

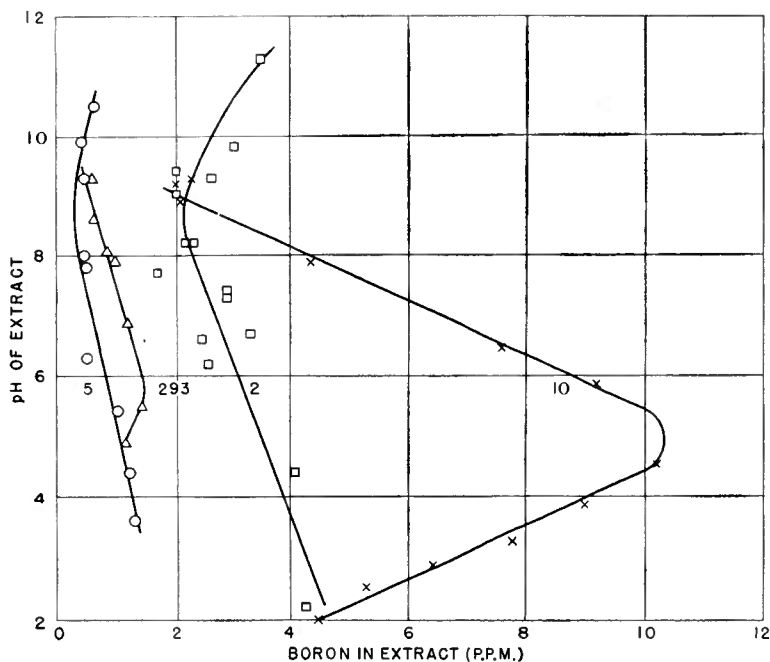


FIGURE 3.—Relation of hydrogen-ion concentration to solubility (and fixation) of boron in soils.

That boron deficiency is more prevalent in alkaline than in acid soils and that it is sometimes induced by the addition of lime is now so well supported by both field and pot-culture observations (3, 9, 20, 24, 26, 27, 30, 38) that little doubt can remain as to the primary facts. Some difference of opinion does exist, however, with respect to the causal mechanism. The idea has been advanced by several that the addition of lime brings about the formation of "insoluble" calcium borates or borate of lime. It is essential to any consideration of this subject that due recognition be given to the fact that the term "insoluble" as applied to chemical compounds and minerals is a relative one. All of the calcium borates for which we have been able to find solubility data are soluble in water to the extent of 50 p. p. m. or more of elemental boron.

Bobko et al. (3) discard the idea that lime additions cause boron to become inaccessible to plants because of chemical precipitation and substitute therefor one of biological fixation. In the fixation tests upon which this conclusion is based the solutions used were relatively high in boron and a fixation of a few milligrams of boron per 100 gm. of soil could easily have been missed. More recently, Naftel (26) has also advanced the suggestion that boron is taken up and held by organisms at higher pH values more suitable for their growth, but he provides no supporting data. Dennis and O'Brien (9) regard boron deficiency in soils as being of two kinds, primary and induced. The deficiency is designated as primary if soils are poor in boron, taking as an example the deficiency in areas of Scotland where brown heart of swedes is prevalent. The poverty of boron in sedimentary rocks of the region was thought to be related to the almost complete absence of tourmaline in the aureoles of the major granitic intrusions. They classify as induced the type of boron deficiency such as that brought on by liming. They call attention to the fact that prior to Brandenburg's experiments (4), showing that boron deficiency was responsible for heart rot of beets, the disease, which is most prevalent on alkaline soils, was assumed to be directly due to excessive alkalinity.

The boron supply of plants, particularly of those growing in soils that are inclined to be deficient, rests on a basis that is highly dynamic. That the rate of solution is an essential consideration, and perhaps one of far more importance than the total supply in the soil, is in a measure illustrated in a number of the tables presented in this bulletin. The fact that the boron requirements of plants are in most instances supplied by low concentrations if these are maintained interposes serious analytical difficulties on any attempt to determine in the laboratory the extent of boron deficiencies of soils. It seems highly probable that the determination of the adequacy of supply will remain one for biological and field-trial methods rather than for chemical measurement. Attempts made to correlate the total or relative amounts of extractable boron with the incidence of deficiency symptoms have met with little success. Woodbridge (39), for example, endeavored to relate the boron recoverable by methyl alcohol distillation from British Columbia soils with that found in the leaves and twigs of apples. He found no correlation between the concentrations of boron in the soil and the incidence of drought spot and corky core. High soil concentrations, induced by additions of either boric acid or borax, were associated with a general freedom from these diseases.

The data presented in figure 3 established by direct chemical methods that there is an outstanding relationship between pH values of soils and the equilibrium concentration of boron in the aqueous phase of soil suspensions. These findings, however, are not wholly specific for the particular point that is now attracting such widespread interest, namely, the effect of liming on boron availability. The liming of acid soils brings about a change in pH value, but it cannot be assumed *a priori* that the effect on boron solubility would be the same as that induced by an equal change in pH value effected by the addition of sodium hydroxide.

For a wholly satisfactory comparison of the effects of liming and treatment with sodium hydroxide one should start with acid soils, but

acid soils were not available with high enough concentrations of soluble boron for measurements by methods described. It has been found necessary, accordingly, to delimit the question. The one an attempt was made to answer may be stated: Does the acidification of limed and unlimed calcareous soils by saturation with carbon dioxide bring about changes in the concentrations of boron in 1-to-1 suspensions that are comparable in magnitude with those that result when the soils are acidified with hydrochloric acid? Conversely, does the precipitation of calcium carbonate by drying soils saturated with carbon dioxide, with resultant increase in pH value, cause a fixation of boron that is disproportionate to that observed when the hydrogen-ion concentration is changed by the addition of sodium hydroxide?

Soils 2, 5, and 10 in 1-to-1 suspensions were treated with carbon dioxide both with and without the addition of 5 percent of calcium carbonate. After aeration and agitation for 48 hours with air free of carbon dioxide in one series and with carbon dioxide in the other, the supernatant solution was quickly filtered. Determinations of boron and calcium were made on the filtrates of the suspensions. A parallel series was treated identically except that the suspensions were not filtered after aeration or carbon dioxide treatment. Instead, while still in Kavalier boron-free flasks, these were placed in a drying oven at 70° C. and dried with the aid of a stream of air directed into each flask. When thoroughly dried the soils were again taken up in a like volume of water and allowed to stand with recurrent shaking for 48 hours.

TABLE 5.—*Effect of aeration and of saturation with carbon dioxide on solubility of boron*

[Determinations on filtrates of 1-to-1 suspensions]

Item	Boron		pH of suspensions		Calcium per liter after aerating or CO ₂ saturation	Electrical conductance (K×10 ⁵ at 25° C.)	
	After CO ₂ saturation	After drying and re-suspending	After aerating or CO ₂ saturation	After drying and re-suspending		After aerating or CO ₂ saturation	After drying and re-suspending
Aerated suspensions:							
Control:	<i>P. p. m.</i>	<i>P. p. m.</i>			<i>Mg. equiv.</i>		
Soil 2		2.86	8.3	8.2	2.71	58	63
Soil 564	7.9	8.1	3.23	50	78
Soil 10		4.37	7.7	8.0	3.83	289	293
Plus CaCO ₃ :							
Soil 2		2.77	8.5	8.1	2.55	56	58
Soil 564	8.0	7.9	2.96	50	76
Soil 10		3.86	8.0	8.1	3.82	290	300
Suspensions saturated with CO ₂ :							
Control:							
Soil 2	3.74	2.74	6.0	8.1	24.4	214	61
Soil 5	1.10	.64	6.1	7.9	19.7	203	72
Soil 10	7.74	4.59	6.0	8.2	8.3	362	289
Plus CaCO ₃ :							
Soil 2	4.08	2.80	6.1	8.0	26.4	225	60
Soil 597	.70	6.0	7.9	20.2	210	71
Soil 10	7.92	4.04	5.9	8.1	14.8	462	295

Saturating the suspensions with carbon dioxide served to reduce the pH values from 8 to 6, to increase up to threefold the concentrations of electrolytes, and almost to double the quantity of boron in solution (table 5). The solubility of the boron in the soils treated with carbon

dioxide was essentially the same after drying and resuspending as that in the parallel treatment where air free of carbon dioxide was used. In other words, the carbon dioxide treatment was without permanent effect on the form of fixation. The boron brought into solution by the carbon dioxide treatment was refixed by absorption or precipitation in forms of the same solubility as those that existed prior to the treatment.

In table 6 a comparison is made between the effects of shifting the pH value of soils with hydrochloric acid and sodium hydroxide and those that result when the pH value is shifted by carbon dioxide saturation and calcium carbonate precipitation. The data of the HCl-NaOH series are interpolated from the graphs of figure 3, and those of the $\text{H}_2\text{CO}_3\text{-CaCO}_3$ series are taken from table 5.

TABLE 6.—Comparison between effects of shifts in hydrogen-ion concentrations in the HCl-NaOH series (fig. 3) and in the $\text{H}_2\text{CO}_3\text{-CaCO}_3$ series (table 5) on concentration of boron in 1-to-1 suspensions

Series and pH value	Boron in filtrates		
	Soil 2	Soil 5	Soil 10
HCl-NaOH series:	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
pH 6	3.2	0.9	8.8
pH 8	2.3	.4	4.3
Difference9	.5	4.5
$\text{H}_2\text{CO}_3\text{-CaCO}_3$ series:			
pH 6	3.74	1.10	7.74
pH 8	2.74	.64	4.59
Difference	1.0	.46	3.15

The two series of measurements were made 6 or 8 months apart, and extraneous differences in treatments or in the temperatures at which the suspensions were held and extracted are indicated by the fact that the boron concentrations of the $\text{H}_2\text{CO}_3\text{-CaCO}_3$ series are somewhat higher at both pH 6 and 8 than those found in the HCl-NaOH series. Difficulty was encountered in extracting the solutions from the soil 10 suspensions without loss of carbon dioxide with a resultant rise in pH value. This soil is heavy, and in suspensions it is rather badly dispersed. It is thought that a rise in pH value would result in some loss of boron by fixation.

It is shown by table 6 that the effects on boron solubility of shifting the pH value of soil suspensions by treatment with hydrochloric acid and sodium hydroxide and by treatment with carbon dioxide and calcium carbonate are essentially alike. It is concluded that the change in boron availability that has been observed to follow the application of lime to acid soils is a function of the change in pH value or of some variable to which hydrogen-ion measurements provide an index. It does not follow that organisms (3) are without any effect on boron availability, but it does seem probable that their direct importance may be a secondary one.

The effects of soil amendments such as lime and sulfur on the conditions resulting from the use of irrigation waters with injurious concentrations of boron merit consideration with the foregoing data on hydrogen-ion concentration.

Irrigation waters as a rule carry calcium and bicarbonate ions in solution. As a result of evaporation and water uptake by plants, carbon dioxide is lost from the soil solution and calcium carbonate is precipitated. The precipitation of calcium carbonate in soils is believed to follow the use of nearly all irrigation waters; with the use of some waters this precipitation may amount to several tons per year. As a consequence of calcium carbonate precipitation as well as other factors it is not uncommon to find that irrigated soils are more alkaline than adjacent unirrigated soils. These high values, which are commonly in the pH 7 to 8 range, are conducive to boron fixation in the soil and to the maintenance of soil-solution concentrations lower than would otherwise be the case. Owing to nutritional disturbances associated with the uptake by plants of nutritive ions, soils giving high pH readings are not usually regarded as suitable for the culture of citrus and other crops as are soils with values of pH 7 or below. So, while boron fixation is favored by low hydrogen-ion concentration, the advantage may be offset in other ways. The addition of lime to irrigated soils will increase soil alkalinity, temporarily at least, and thereby tend to reduce the concentration of boron in the soil solution by fixation; but the use of lime on alkaline soils as a means of lessening boron injury cannot be recommended.

Applications of sulfur, depending on the quantity used and the oxidizing, buffering, and other conditions of the soil, can be expected to lower the pH values in soils. Following an effective action of sulfur, higher boron concentrations in the soil solution can be expected as a result of a reduced rate of fixation and the dissolution of some of the previously fixed boron. With the higher boron concentrations in the soil solution additional boron injury will be brought about if the land is planted to a boron-sensitive crop.

The reclamation of soils containing injurious concentrations of boron may be effected by leaching boron from the root zone by the use of sufficient quantities of water. Increasing the acidity of the soil by the addition of sulfur to the land should hasten this process. The use of sulfur as an aid to reclamation might prove practicable in some instances if better waters are to be substituted and if the land is not planted to permanent crops.

EFFECT OF TEMPERATURE ON SOLUBILITY

It is shown by the data of table 7 that soil boron, like boron compounds generally, is substantially more soluble at high than at low temperatures. The measurements were made on 1-to-1 suspensions of stock soil 2 in dilute calcium sulfate solutions. These were held at the indicated temperatures for 2 hours and the supernatant liquid then siphoned off and filtered. The flasks were shaken frequently during the first hour and allowed to settle during the second. Between a temperature of 21° C. and boiling there was a threefold increase in the concentration of boron in the aqueous phase.

In related experiments it has been found that much or perhaps all of the boron brought into solution as a result of high temperature may be reabsorbed by the soil when cooled and allowed to stand. Suspensions of soil 2 were boiled under a reflux condenser for 1½ hours and allowed to settle at a temperature just below boiling for half an hour. One of the suspensions was filtered while hot. It contained

4.96 p. p. m. of boron. The second was cooled in a water bath rather quickly and then filtered. This filtrate contained 3.43 p. p. m. of boron.

TABLE 7.—*Solubility of soil boron as influenced by temperature*

[Stock soil 2 in 1-to-1 suspensions of 0.005-N CaSO_4]

Temperature (° C.)	Electrical con- ductance ($K \times 10^3$ at 25° C.)	Boron
		<i>P. p. m.</i>
6	97.4	1.40
21	98.4	1.61
25	99.7	1.72
30	101.0	1.96
35	99.8	2.18
46	99.1	2.63
Boiling	105.0	4.96

Suspensions of soil 1 left overnight in an oven at 59° C. and then set aside until they reached room temperature contained the same amount of boron on filtration as suspensions that were not heated. The heated pair had solution concentrations of 0.24 and 0.21 p. p. m. and the unheated pair 0.24 and 0.20 p. p. m.

The fact that the concentrations of boron in the aqueous phase of suspensions tend to be unchanged after heating and then being allowed to cool for a sufficiently long period suggests that the boron brought into solution by heat returns to its original form of combination when cooled, otherwise some difference in solubility would be expected.

RATE OF DISSOLUTION OF SOIL BORON

The boron found in the soil solution of 10 western soils constituted only a very small proportion of that which could be removed by prolonged leaching or by several other methods of extraction (table 10). Less than 1 percent of the total boron that could be extracted by acids was present in the soil solution of a number of the soils.

The rate at which boron comes into solution has important agricultural implications. The adequacy of the boron supply in soils is determined not alone by the concentrations that result in soil solutions when the aqueous and solid phases are in equilibrium as a result of long standing, but also by the rate at which boron in solution is replaced after removal by leaching or by plant uptake. A similar consideration is involved in reclamation of high-boron soils by leaching. A number of light applications of water used to remove boron from soils may be more effective than the same amount of water applied in one or two heavy applications that pass through the soil rapidly.

The rate of solution of boron in soils is illustrated by the data of table 8 and also, though less directly, elsewhere in this bulletin. The experiment was conducted in a basement vault where temperature conditions were relatively constant. Four kilograms of air-dried soil and a bottle containing 16 liters of 0.005-normal calcium sulfate solution were allowed to come to temperature equilibrium by standing overnight. The following morning the experiment was started by adding the soil to the solution and shaking vigorously for 5 minutes,

after which approximately 600 ml. of the suspension was poured on a paper filter for the first measurements. Succeeding samples were collected in like manner at intervals over a period of 1 year, and finally a last sample was taken after 5 years had elapsed. During the final 4 years the bottle was shaken only a few times. The boron determinations represent duplicate electrometric titrations. The pH measurements were made colorimetrically on the filtered extracts. Boron dissolved from the soil is expressed in terms of the concentrations in the 1-to-4 extracts and also in terms of milligrams of boron per kilogram of soil. This soil, a Hanford sandy loam from the San Joaquin Valley, had been irrigated for a number of years with water containing approximately 3 p. p. m. of boron.

TABLE 8.—*Effect of time on dissolution of boron from soils*

(Stock soil 2 in a 1-to-4 suspension)

Elapsed time	Temperature	pH of extract	Conductance ($K \times 10^3$ at 25° C.)	Boron		Elapsed time	Temperature	pH of extract	Conductance ($K \times 10^3$ at 25° C.)	Boron	
				Solution concentration	Referred to dry weight of soil					Solution concentration	Referred to dry weight of soil
				P. p. m.	Mg. per kg.					P. p. m.	Mg. per kg.
5 minutes....	24	7.3	67.8	0.54	2.16	14 days....	23	7.6	78.1	1.07	4.28
10 minutes....	24	7.3	69.1	.60	2.40	21 days....	24	7.5	80.9	1.12	4.48
20 minutes....	24	7.3	69.0	.64	2.56	28 days....	24.5	7.5	82.6	1.12	4.48
1 hour.....	23	7.3	69.2	.68	2.72	6 weeks....	26	7.5	86.2	1.21	4.84
2 hours.....	23	7.3	69.5	.69	2.76	12 weeks....	26.3	7.5	94.6	1.35	5.40
4 hours.....	23	7.4	70.3	.72	2.88	18 weeks....	25	7.7	98.6	1.35	5.40
8 hours.....	23	7.2	71.7	.81	3.24	34 weeks....	24.8	7.5	108	1.41	5.64
1 day.....	23.5	7.3	71.8	.84	3.36	42 weeks....	21	7.4	116	1.50	6.00
2 days.....	23.5	7.6	73.2	.93	3.72	52 weeks....	24	7.6	107	1.54	6.16
4 days.....	24	7.1	73.2	.90	3.60	5 years....	21.5	8.0	127	1.59	6.36
7 days.....	24	7.5	75.8	.96	3.84						

¹ These samples stood open overnight before the pH value was determined.

Much boron was brought into solution during the initial 5-minute period; thereafter the rate of release diminished rapidly, but some additional amounts were continuously released throughout the first year. The quantity of boron released during the last 4 years of the test was about the same as that released during the last 10 weeks of the first year.

To reach equilibrium with 4 parts of water, there was dissolved from this soil 6.16 mg. of boron per kilogram. The solution phase at equilibrium contained 1.54 p. p. m. of boron. In another experiment this soil when wetted with 11.9 percent of moisture released 1 mg. of boron per kilogram of soil and equilibrium between the aqueous and solid phases was established in 2 days. The soil solution at this equilibrium contained 7.83 p. p. m. of boron.

FIXATION AND RELEASE OF BORON BY SOILS CONTINUOUSLY SATURATED WITH WATER

When a solution containing boron is passed through a soil, fixation may be expected to occur if the concentration of boron in the leaching solution exceeds that of the soil solution with which equilibrium conditions had previously been established, provided, of course, that

temperature, hydrogen-ion concentrations, and other pertinent conditions remain constant. If, on the other hand, there is less boron in the leaching solution than in the previous soil solution, a release of boron should result. Irrespective of the direction of the change, a new equilibrium concentration will eventually be established, after which the concentration of boron in the leaching solution will be substantially unchanged as it passes through the soil. Any alteration, then, in the concentration of the solution in contact with a soil results in a change in the quantity of boron that is fixed.

These effects are illustrated by the data of table 9. In this experiment 2-kg. portions of stock soils 1 and 2 were placed in a series of Oldberg-type percolator tubes in a basement room where temperature conditions were fairly uniform. The soils were repeatedly leached with successive volumes of solution, the volume of each solution being equal to the water-retaining capacity of the soil as held in the tubes above a small wad of glass wool. In the instance of soil 1 this was 550 ml., and of soil 2, 650 ml. The columns of soil were approximately 30 cm. in depth, over which the solutions, when newly applied, formed columns of 9 to 11 cm. in height.

The soils were first leached 15 successive times with distilled water containing 10 mg. equivalents per liter of calcium sulfate to maintain permeability. As the second phase of the experiment, leaching was continued with calcium sulfate solutions containing boron, and as the third phase, boron-free calcium sulfate solutions were used.

During the second phase of the experiment, soil 1 removed 0.70 mg. of boron from solutions containing at first 0.5 and then 1 p. p. m. of boron, and 2.32 mg. from solutions containing at first 2.5 and then 5 p. p. m. Substantially the same quantities of boron were released by this soil during the third phase of the experiment when leached with boron-free solutions as were fixed during the second phase while being leached with solutions containing boric acid.

Soil 2 contained substantially more readily soluble boron than soil 1, but the boron-release and boron-fixation characteristics of the two soils proved to be essentially the same. The phase-1 leachings of soil 2 were not continued to as low concentrations as were the phase-3 leachings, and somewhat more boron was recovered during the final release from tubes 5 and 6 than was fixed during the second phase.

At the start of the first and third phases boron was released from both soils in relatively large amounts, but through successive leachings the rate decreased sharply and finally flattened out. The second-phase fixations proceeded rapidly at first, much boron being removed from the first few solutions, but throughout fixation decreased until the solutions passed through the soils unchanged.

The curves of fixation and release, as may be observed from the data, are essentially alike. Boron was fixed by the soil or released to solution only as the concentrations of the leaching solutions exceeded or fell below some equilibrium ratio. These observations are in accord with those shown in figure 2, where each increase in solution concentration was accompanied by further adsorption; but for the successive units of boron fixed, proportionately greater solution concentrations were required; i. e., the ratio of boron in the aqueous phase to that adsorbed became greater.

TABLE 9.—Release and fixation of boron by stock soils 1 and 2 during leaching with boron-free and dilute boron solutions

Soil and solution		Boron in percolate No.—															Total boron		
		FIRST PHASE—SOILS LEACHED WITH BORON-FREE SOLUTION ¹															Added	Passed	Fixed
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15			
Soil 1, tubes 1-4 Soil 2, tubes 5-8		P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	Mg. per kg.	Mg. per kg.	Mg. per kg.
		0.62 7.50	0.31 3.23	0.26 1.95	0.15 1.14	0.11 0.77	0.11 0.58	0.12 0.70	0.07 0.46	0.08 0.40	0.05 0.27	0.05 0.30	0.05 0.29	0.11 0.41	0.08 0.25	0.05 0.24	0.05	0.05	0.69 5.87
Soil 1: Tubes 1 and 2: Leaching solution 0.5 p. p. m. boron Leaching solution 1 p. p. m. boron Tubes 3 and 4: Leaching solution 2.5 p. p. m. boron Leaching solution 5 p. p. m. boron		SECOND PHASE—LEACHING CONTINUED WITH SOLUTIONS CONTAINING ADDED BORON ¹															Mg. per kg.	Mg. per kg.	Mg. per kg.
		16	17	18	19	20	21	22	23	24	25	26	27	28	29	30			
Soil 2: Tubes 5 and 6: Leaching solution 0.5 p. p. m. boron Leaching solution 1 p. p. m. boron Tubes 7 and 8: Leaching solution 2.5 p. p. m. boron Leaching solution 5 p. p. m. boron		P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	Mg. per kg.	Mg. per kg.	Mg. per kg.
		0.06 0.34	0.09 1.67	0.25 2.01	0.36 2.23	0.32 2.00	0.37 2.11	0.43 2.32	0.46 2.36	0.53 2.52	0.57 3.19	0.76 4.39	0.92 4.81	1.00 4.77	1.02 4.90	0.90 4.81	2.00	2.20	0.70
Soil 1: Tubes 1 and 2: Leaching solution 0.5 p. p. m. boron Leaching solution 1 p. p. m. boron Tubes 3 and 4: Leaching solution 2.5 p. p. m. boron Leaching solution 5 p. p. m. boron		0.16 0.26	0.20 1.06	0.18 1.50	0.27 2.02	0.28 1.92	0.31 2.08	0.39 2.31	0.45 2.36	0.48 2.46	0.46 2.88	0.56 3.93	0.83 4.51	0.83 4.53	0.94 4.92	1.05 5.15	3.40	2.38	1.02
		0.26 0.31	1.06 1.50	1.50 2.02	2.02 2.02	1.92 2.08	2.08 2.31	2.31 2.36	2.36 2.46	2.46 2.88	2.88 3.93	3.93 4.51	4.51 4.53	4.53 4.92	4.92 5.15	5.15 5.15	17.11	13.50	3.61
Soil 1: Tubes 1 and 2: Tubes 3 and 4: Soil 2: Tubes 5 and 6: Tubes 7 and 8		THIRD PHASE—LEACHING CONTINUED WITH BORON-FREE SOLUTION ¹															Mg. per kg.	Mg. per kg.	Mg. per kg.
		31	32	33	34	35	36	37	38	39	40	41	42	43	44	45			
Soil 1: Tubes 1 and 2: Tubes 3 and 4: Soil 2: Tubes 5 and 6: Tubes 7 and 8		P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	P, p. m.	Mg. per kg.	Mg. per kg.	Mg. per kg.
		0.87 4.06	0.33 1.96	0.33 1.43	0.26 0.80	0.10 0.56	0.14 0.47	0.14 0.22	0.14 0.37	0.10 0.30	0.08 0.15	0.06 0.17	0.05 0.14	0.05 0.12	0.05 0.12	0.05 0.16	0.05	0.05	1.44 3.75

¹ Solutions containing the appropriate concentrations of boron were used to displace percolates numbered 15. These solutions came through as percolates numbered 16. Likewise, boron-free solutions were used to displace percolates numbered 30.

RECOVERY OF BORON FROM SOILS BY WATER, ACID, AND ALKALI EXTRACTION

Fusion analyses, which are so extensively employed in studies of the composition of minerals and soils, have been tried in only a limited way in these boron investigations. The reasons for neglecting the use of this method for appraisals of the total quantity of boron in soils have been twofold. On the one hand there are analytical difficulties consequent upon the fact that soils contain proportionately little boron, and, on the other, only a limited agricultural significance can be attached to the information when gained. Assume that a soil does contain as much as 50 p. p. m. of boron, and that one starts with 5 gm. of it for a fusion analysis; by the time fusion has been completed and the carbonate has been neutralized, the resulting mass of salt will weigh in the order of 50 gm. The 0.25 mg. of boron assumed to be present must be separated from this mass. The conventional procedure is a distillation with methyl alcohol while the system is acid and nearly anhydrous. There is reason to believe that boron is not lost by volatilization during fusion, but an important question exists in regard to the removal by the distillation method of the whole of what amounts to little more than a trace of boron from such a mass of salt. For the method to be of any value for the determination of small quantities of boron, the sodium carbonate and acid, which are used in large quantities, must be free from boron.

Fusion analyses of soil 5, for which extractions by other methods are reported in table 10, have yielded quantities of boron ranging from 28 to 58 p. p. m. The higher value was obtained by a direct titration of boron without methyl alcohol distillation. Analyses by direct titration following fusion and the removal of iron and aluminum were made on a soil ground in a mill in the presence of 0.1-normal sodium tetraborate. After washing the soil, and prior to fusing, 1 mg. of boron was added to a second 1-gm. aliquot. Approximately a 90-percent recovery of the added boron was secured, the values from the respective samples being 270 and 1,200 p. p. m.

The store of boron of soils that is of greatest agricultural significance is not that of the interior of refractory soil minerals but rather that in the form of undecomposed plant remains, that in precipitated inorganic compounds, and that adsorbed or chemically combined on or near the surface of the soil particles. It is boron from these latter sources, even though of low solubility, that replaces boron lost from the soil solution by leaching and by removal by plants. Boron deficiency in soils in the majority of cases probably represents lack of availability, either physical or chemical, as often as it does insufficient total supply. The injurious concentrations of boron that persist in irrigated lands after good waters are substituted for high-boron waters reflect the dissolution of boron held in forms of low solubility that has been recently fixed.

For several reasons it has seemed that measurements of the amounts of labile and semilabile boron of soils might possess a greater agricultural significance than measurements of the total boron in soils. Proceeding with this viewpoint, each of the 10 stock soils was subjected to several extraction treatments, some of which were severe in character. These treatments included repeated leaching with cold water, extraction with hot water, extraction with hot water after

burning out the organic matter in the presence of sodium carbonate, extraction with 0.5-normal hydrochloric acid followed by washing with hot water, and extraction with acid after ignition in the presence of sodium carbonate. For purposes of comparison and contrast there are included with this series the results obtained by the displacement of soil solutions. The extraction procedures were applied to each of the 10 stock soils. The results of the measurements are reported in table 10.

Soil-solution displacements, method 1, will receive additional consideration later; it is believed to represent the best-known appraisal of the quantity of boron in the soil solution when approximately a moisture-equivalent percentage of water is present.

TABLE 10.—*Recovery of boron from soils by extraction with water and with acid and by extraction after igniting with sodium carbonate*

Method	Recovery of boron (per kilogram of soil) from stock soil No.—									
	1	2	3	4	5	6	7	8	9	10
Soil solutions:	<i>Mg.</i>	<i>Mg.</i>	<i>Mg.</i>	<i>Mg.</i>	<i>Mg.</i>	<i>Mg.</i>	<i>Mg.</i>	<i>Mg.</i>	<i>Mg.</i>	<i>Mg.</i>
1. Displacement	0.06	1.00	0.15	0.38	0.26	0.08	0.16	0.14	0.11	1.41
Aqueous extracts:										
2. Sum of 20 cold-water percolates	.54	5.89	1.35	1.22	.69	1.36	2.15	1.81	1.46	14.42
3. Sum of 3 hot-water extractions	.79	5.39	1.42	2.41	2.15	1.28	2.32	1.72	1.58	13.49
4. Sum of 7 to 20 hot-water extractions	.98	6.94	2.04	2.92	4.25	2.02	3.89	3.17	2.18	18.90
Alkali extracts:										
5. Ignited with Na_2CO_3 , followed by 3 hot-water extractions	1.66	5.24	2.60	-----	4.88	4.35	2.11	7.84	4.52	12.14
Acid extracts:										
6. 2 hot 0.5-N HCl and 3 hot-water extractions	.60	3.78	1.20	-----	4.08	1.38	1.14	3.24	1.56	12.17
Alkali-acid extracts:										
7. Ignited with Na_2CO_3 , followed by water and acid extractions	1.94	5.39	3.26	3.95	9.65	5.95	2.63	11.40	4.39	9.84
8. Same soil, acid extractions repeated	.94	1.63	1.38	2.00	2.94	1.63	1.50	4.01	2.44	4.39
9. Same soil, acid extractions again repeated	.75	.88	.63	1.13	1.13	.00	.06	2.26	1.94	3.82
10. Same soil, reigned with Na_2CO_3 and again extracted with acid	.25	.75	.94	.50	.81	3.01	1.50	1.44	3.63	5.26
11. Sum of recoveries by steps 7, 8, 9, and 10	3.88	8.65	6.21	7.58	14.53	10.59	5.69	19.11	12.40	23.31

Under the first of the aqueous extractions, method 2, there is reported the total boron removed by 20 successive leachings with volumes of water equal to the saturation percentages of the respective soils. In each instance 2 kg. of soil was used in Oldberg-type percolator tubes. The permeability of the soils was such that several days, or sometimes a week, was required for a single percolate to pass. The progress of leaching of each of the 10 soils was kept in pace so that the time factor would be the same for all.

The hot-water extractions, methods 3 and 4, were made by stirring 500 gm. of soil with 250 cc. of water for 20 minutes while in place on a 111-mm. Buechner funnel arranged in a water jacket. The filter paper was protected by a screen wire. Filtration was prevented during the 20-minute period by keeping the suction valve closed. The sums of three successive extractions and of n successive extractions are reported. In the latter case the extractions were repeated until the concentration of boron in the extracts had decreased to

0.07 or 0.08 p. p. m. Temperatures at or near boiling were maintained during the extractions.

The ignitions in the presence of sodium carbonate, method 5, were made as follows: Fifty gm. of air-dry soil was transferred to a platinum dish after mixing intimately with 2.5 gm. of Na_2CO_3 . Distilled water was added from a wash bottle without stirring until a little free water appeared at the margins. The soil was then baked in a muffle at dull red heat until the organic matter was destroyed. The soil, when cool, was pulverized in a mortar and then extracted three times with 25 ml. of hot distilled water, each being brought to boiling temperature. The values for these combined hot-water extracts, after ignition with sodium carbonate, all fell in the range pH 10.5 to 11.3. When acid extractions, methods 7 to 11, followed ignition with sodium carbonate, the soil was first extracted twice with 50-ml. portions of water, each being brought to a boil. The filtrates were combined with those from the subsequent acid extractions, the methods for which are outlined in the following paragraph.

In the acid extractions, method 6, two successive 50-ml. portions of 0.5-normal hydrochloric acid for 50 gm. of soil were used. After adding the first acid to the soil in a Kavalier Erlenmeyer flask, the suspension was brought just to boiling and filtered while hot through a filter paper. The filter paper and soil were then returned to the flask and reextracted with a second portion of acid. This second acid extraction was followed with one 50-ml. and two 25-ml. hot-water extractions, boiling each while shaking and then decanting through a filter into the original acid filtrates, which were collected in a 460-ml. Kavalier beaker. Lead nitrate clarification prior to the direct titration of the boron was necessary to remove interfering materials such as phosphate, aluminum, and iron brought into solution by the acid extraction. For this the filtrates were made acid to bromthymol blue, if not already so, with 2-normal sulfuric acid and 2.5 ml. of normal lead nitrate added. The solution was then made alkaline to phenolphthalein with concentrated sodium carbonate solution and made up to 300 ml. After filtration a 250-ml. aliquot was used for the electrometric titration of the boron.

The boron present in the soil solutions (method 1) of these 10 soils represented from 7 to 38 percent of that obtainable by 20 cold-water leachings (method 2). From 8 of the soils substantially the same quantity of boron was obtained by 3 hot-water extractions (method 3) as by the 20 successive leachings with cold water. Hot water was disproportionately effective in the removal of boron from soils 4 and 5. The consistency between the sum of the first 3 hot-water extracts and the sum of upward to 20 hot-water extracts is not very close. The alkali extractions, method 5, and acid extractions, method 6, gave results that point to further diversity in the forms of the boron combinations in these soils. For the most part the acid extractions were not as effective as the water extractions, method 5, which followed the treatment with sodium carbonate. A combination of the treatments, methods 7 to 9, was more effective than either alone in most but not all soils. Reignition after acid extraction liberated much additional boron from soils 6 and 7, but in other cases it appears that substantially the same amounts might have been obtained by a continuation of the acid extractions.

The treatment with acid should, on theoretical grounds, have brought into solution some silica from silicate minerals, possibly borosilicates; but on standing or on heating in an acid solution there is a strong tendency for silica to form a gel, which might remove boron from solution. How much of either type of action is involved in these acid extractions the writers have not endeavored to determine. The dissolution of soil silicates should tend to bring boron into solution, but likewise the reprecipitation of silica would be expected to remove boron from solution.

Silicate minerals generally tend to be at least slowly soluble in highly alkaline solutions. An interest in the boron of soil-forming minerals which is present on or near the surface of soil particles made the possibilities of alkali extraction appear somewhat promising as a means of appraising labile and perhaps potentially labile boron of the soil. As is well known, however, the filtration of soils with alkaline solutions is not easily accomplished, not only because of the dispersing action of the alkali on soil colloids, but also because organic matter gelatinizes and becomes soluble and sodium silicates cause trouble. Digesting the soil with aqueous solutions of calcium oxide was tried with some promise, but the alkali extractions made the electrometric titration of the boron uncertain. The procedure of igniting soils in the presence of sodium carbonate, method 5, was tried as an alternate procedure, and as far as laboratory manipulation and the boron determination are concerned it is straightforward and does not cause any difficulty. The procedure, however, is highly destructive of the soil, and for this reason the interpretative significance of the resulting values is open to question.

These results have served to bring out the fact that the forms in which boron is held in any one soil and in different soils are highly diverse. Uncertainty must accompany the interpretation of any estimate of the potentially labile boron in soils.

BORON IN SOIL SOLUTIONS

DISPLACED SOIL SOLUTIONS

This and some of the succeeding sections will deal with the concentrations of boron in soil solutions. Emphasis will be placed almost wholly on boron as a toxic rather than as an essential element. Plant tests seem generally better suited than chemical analyses to the measurement of the availability of boron in deficient soils. This latter problem has a highly dynamic basis, since the rate of uptake from deficient soils is largely governed by rate of dissolution. The soil-solution concentration of a soil at static equilibrium is not necessarily at all representative of the concentration during uptake by plants. Also, there is no reason to assume that there is a good parallelism between rate of release of boron during uptake and concentrations at static equilibrium.

It is not intended to imply that under high-boron conditions there is not an almost constant exchange of boron between soil and solution. Drying, irrigation, plant uptake, and leaching all tend to alter the concentrations in the solution phase. The changes are followed by the reestablishment of equilibrium. The boron from irrigation waters that has been fixed by soils is presumably on the surface and therefore physically available. This boron, for the most part at least,

should be regarded as labile. As may be observed in connection with the data of table 10, the ratio of the total boron soluble in cold water to the boron present in the soil solution tends to be relatively high. Major trends in the concentration of boron in soil solutions of irrigated soils will therefore proceed rather slowly. Abrupt changes in concentration such as might follow rains or irrigation are apt to be of short duration.

The injury produced by boron to plants in sand cultures has been shown (12) to be closely related to uptake and accumulation, and these in turn to the concentrations of boron in nutrient solutions. As a basis for the investigation reported here, it was assumed at the outset that injury in the field was likewise closely correlated with the concentration of boron in the soil solution. To establish that very close correlations exist between the injury of field plantings and boron in soil solutions in areas where many soil types are represented is naturally difficult. Such an undertaking is complicated not only by the fact that a number of variables are known to influence boron uptake, but also by reason of the unequal horizontal distribution of both boron and roots in the successive soil horizons.

Investigators are in general agreement that analyses of the displaced solutions from soil samples constitute the best available approach to a knowledge of the composition of soil solutions under field conditions. How closely the one represents the other is sometimes controverted, but a better procedure has not been developed.

The methods followed in the displacement of the soil solution here reported have been essentially those of Burd and Martin (5). Some of the heavier soils puddled badly during packing in the displacement tubes when previously wetted with as much as a moisture equivalent of water, in which event displacement was excessively slow. In wetting soils it was found advantageous to screen them as they came from the field or after drying and then spread them out in a sheet 4 or 5 mm. thick on a metal table top. When the soil was so spread, the desired amount of water was sprinkled on evenly and the wetted soil left overnight under an oilcloth before being moved. Wetted in this manner, the soils could be handled with much less danger of puddling. The method and density of packing the soils in displacement tubes was found to be of material importance, not only from the standpoint of the time required to displace sufficient solution for analysis but also from that of channeling, i. e., the mixing of the displacing with the soil solution. Those who have undertaken displacements are familiar with the latter difficulty. A flat-faced tamper with a diameter a few millimeters less than that of the displacement tube was used. Successive 100- to 200-gm. portions of the soil were firmed into place by five or six strokes with the tamper. A very thin coat of waterproof grease, applied to the insides of the tubes before packing, was found to be advantageous. The displacement tubes are made of seamless brass tubing, 17 inches long and 3 inches outside diameter. These tubes are fitted with screw caps at each end. The upper cap attaches to the air line and the lower cap has a removable disk with a tubular opening. A filter paper and a screen are placed above this disk.

It is well known that many soils, particularly those containing adsorbed sodium, are less permeable to distilled water than to solutions of electrolytes. Soils packed in displacement tubes have been ob-

served to start yielding solutions at satisfactory rates and then slow up after the distilled water had penetrated into and leached the upper end of the soil column. To overcome this effect, 0.2-normal potassium sulfocyanate was used in the later portions of this work as the displacing solution. Not only does this solution promote a more rapid displacement of the solution from many soils, but it provides a highly sensitive color test for channeling.

EXTRACTIONS AT LOW MOISTURE CONTENT

The displacement of soil solutions is at best a slow and often tedious process, and, in addition to special equipment, there are minor matters of technique that are essential to success. As a result, it has seemed highly desirable that an alternative means of appraising the concentration of boron in soil solutions should be worked out for practical use, even though something in accuracy might be lost. In giving consideration to various courses, account has been taken of the fact that only a small part of the total labile boron of soils is customarily present in the soil solution of irrigated lands and that, upon removing a little boron by light leaching, soils commonly tend to reestablish the former boron concentrations. In view of this behavior of boron in soils, it seemed possible that about the same concentrations of boron might be found in solutions from soils wetted just to the moisture equivalent or field-holding capacity and in those wetted with one and one-half or even two times as much water. If so, drawing off for boron determination a portion of the excess water in a pressure filter or on a Buechner funnel would become a relatively simple and straightforward method (12). The results of an extensive series of trials of displacements and of various methods of extraction that were followed through systematically with the 10 stock soils are summarized in table 11.

Both the moisture equivalents (percentages) and the saturation percentages are shown for each of the 10 soils. Extractions based on saturation percentages were used in the initial study for the reason that many laboratories do not have moisture-equivalent centrifuges. It so happens that a 1-to-2 relationship tends to exist between the moisture-equivalent and the saturation percentages of fine-textured soils and those without much sand, but light soils with moisture equivalents of 12 or less are apt to have saturation percentages that are disproportionately high.

The data of table 11 show that in general, but not always, enough boron is dissolved from soils to bring the concentration in $\frac{3}{4}$ -saturation percentages of moisture to substantially as high levels as that of the soil solutions with moisture-equivalent percentages of moisture. In this series, soils 2 and 4 did not release enough boron to the $\frac{3}{4}$ -saturation percentage solutions to bring them up to a satisfactory agreement with the concentrations of displaced solutions. It is to be particularly noted, however, that both of these soils were light and that the saturation percentages were substantially more than twice the moisture equivalent.

Neither full-saturation extracts, dry-soil percolates, nor hot filtrations give results as promising from the standpoint of a practical method as the $\frac{3}{4}$ -saturation percentage extracts; and the last, because of the type of result that may frequently occur when soils are

light, here illustrated by soils 2 and 4, are not as generally suitable as 1.5 moisture-equivalent extracts. If moisture-equivalent percentages cannot be determined, light soils should be wetted with only a half or less of the saturation percentages. Wetting air-dried soils for 2 days and allowing them to stand in closed jars at room temperature gave essentially as high concentrations of boron in the aqueous phase as longer standing.

TABLE 11.—Concentrations of boron in displaced soil solutions and various types of aqueous extracts

Soil No.	Soil class	Moisture equivalent ¹	Saturation percentage ²	Solution concentrations									Hot-water filtrates, 1 soil to ½ water ⁵
				Displaced soil solution ³		Free-water extracts ⁴						Dry soil percolate ⁵	
						Three-fourths saturation		Full saturation					
								Wetted about 2 hours	Wetted 6 days	Wetted 15 days			
				Wetted 2-7 days	Wetted 200 days	Wetted 2 days	Wetted 6 days						
1	Sandy loam	Percent	29.1	P.p.m.	P.p.m.	P.p.m.	P.p.m.	P.p.m.	P.p.m.	P.p.m.	P.p.m.	P.p.m.	
2	do	8.4	29.1	0.70	0.69	0.71	0.65	0.25	0.40	0.35	0.32	1.02	
3	do	11.9	31.3	7.83	7.94	5.14	5.78	2.76	5.01	5.21	6.58	7.50	
4	do	14.1	30.2	1.13	.97	1.37	.98	.40	.70	.73	.76	1.88	
5	Clay loam	11.5	28.3	3.33	3.45	2.34	2.41	1.26	2.35	2.28	2.85	3.45	
6	Sandy loam	21.2	41.9	1.19	1.15	1.19	1.08	.40	1.11	1.15	.70	2.42	
7	Clay	12.2	32.9	.76	.84	1.06	1.07	.50	1.04	.87	.73	1.54	
8	Clay loam	22.5	46.8	.97	1.02	1.04	1.08	.48	.97	.84	.62	2.92	
9	Clay	22.3	46.5	.76	.97	.69	.99	.42	.65	.83	.62	1.96	
10	do	17.4	35.7	.78	.63	.90	.82	.35	.42	.36	.53	2.00	
	Average	21.3	44.3	6.62	6.01	6.30	6.91	3.76	5.42	5.71	4.28	15.80	
				2.40	2.36	2.07	2.17	1.06	1.81	1.83	1.80	4.05	

¹ Moisture equivalent determined by standard methods.

² Water to saturate, or the "saturation percentage," represents the weight of water that must be added to 100 gm. of soil while stirring and tapping to produce a glossy surface. At the saturation percentage the soil has been mechanically puddled and the voids filled with water.

³ Displaced soil solutions were obtained from soils wetted for the indicated periods with approximately a moisture-equivalent percentage of water. After wetting, the soils were allowed to stand for 2 days or longer before displacement. The soil indicated as wetted for 200 days had been held in closed mason jars in a basement vault for about 7 months.

⁴ Free-water extracts are solutions taken from soils wetted for the periods shown with the indicated quantities of water.

⁵ Dry soil percolates represent the percolate from 2 kg. of dry soil packed in Oldberg-type percolators. Water is added to the top of the soil until a saturation percentage of percolate is recovered.

⁶ Hot-water filtrates are from soils wetted with half their weight of water, held at boiling temperature for 20 minutes, and then filtered on a heated Buechner funnel.

The quantities of boron extracted by the several methods, in terms of dry weight of soil, are shown in table 12.

To carry further the inquiry on the relationship between boron concentrations in the displaced solutions and in 1.5-moisture-equivalent extracts, both measurements were made on a series of 20 soil samples that came from areas in which boron injury was under observation. These results are reported in table 13. Higher concentrations were found in displaced solutions than in extracts in 14 of the 20 samples. The fact that 6 of the samples yielded higher concentrations of boron in the extracts than in displaced solutions is probably not due wholly to accidents of the measurements. The 4 samples, 295 to 298, were from the same orchard. The higher boron concen-

trations might be a result of biologically induced differences in hydrogen-ion concentration related to differences in moisture content while standing, and there is also to be recognized the possibility of differences in the temperatures that prevailed when the extractions and displacements were made. Some of the departures between the two methods are greater than might be wished, but in view of the practical advantages served by the 1.5-moisture-equivalent method its use has appeared to be justifiable.

TABLE 12.—*Boron in displaced solutions and in various types of extractions*

[Referenced to the dry weight of soil. For explanation, see table 11]

Soil No.	Soil class	Boron in displaced solution, 2-7 days	Boron in free-water extracts			
			Three-fourths saturation, 2 days	5 X saturation, 2 days	0.5-to-1 hot filtrates	
					First	Sum of <i>n</i> extractions ¹
		<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
1	Sandy loam	0.06	0.18	0.20	0.51	0.98 (7)
2	do	1.00	1.37	2.83	3.75	6.94 (15)
3	do	.15	.35	.53	.94	2.04 (11)
4	do	.38	.46	1.22	1.73	2.92 (10)
5	Clay loam	.26	.42	.69	1.21	4.25 (20)
6	Sandy loam	.08	.30	.56	.77	2.02 (12)
7	Clay	.16	.41	.87	1.46	3.89 (17)
8	Clay loam	.14	.24	.49	.98	3.17 (16)
9	Clay	.11	.24	.62	1.00	2.81 (14)
10	do	1.41	2.09	5.76	7.90	18.98 (20)
	Average	.38	.61	1.38	2.03	4.80

¹ Figures in parentheses indicate the number of successive hot extractions included in the sum.TABLE 13.—*Relationship between boron concentrations in displaced solutions and in 1.5-moisture-equivalent extracts*

Soil No.	Moisture equivalent	Boron in—		Soil No.	Moisture equivalent	Boron in—	
		Displaced solutions	1.5-moisture-equivalent extracts			Displaced solutions	1.5-moisture-equivalent extracts
	<i>Percent</i>	<i>P. p. m.</i>	<i>P. p. m.</i>		<i>Percent</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
291	15.8	1.60	1.43	316	23.6	4.78	3.64
292	9.1	3.18	3.50	317	22.0	.30	.24
293	16.1	1.83	1.99	318	23.0	.80	.66
294	25.0	1.63	1.34	319	24.3	.64	.46
295	12.5	1.34	1.55	320	20.7	1.20	.95
296	13.3	1.32	1.51	321	18.8	.98	.86
297	17.4	.76	.95	322	19.3	1.45	1.16
298	16.4	1.50	2.00	327	16.1	1.94	1.52
313	19.9	3.20	2.87	324	14.7	1.51	1.00
314	21.7	2.36	2.12				
315	21.6	3.07	2.52	Average		1.77	1.61

REPRODUCIBILITY OF 1.5-MOISTURE-EQUIVALENT EXTRACT MEASUREMENTS

There are set forth in table 14 the results of a series of triplicate 1.5-moisture-equivalent extractions of a group of 40 soils. Duplicate extractions were made at the end of what is designated as an 18-hour period, and the third sample after it had been allowed to stand wetted

for 7 days. The 18-hour samples represent soils that were wetted and mixed during the course of an afternoon and extracted in pressure filters the following morning. The quantity of soil taken for each sample was such that 50 percent of the moisture-equivalent percentage would be equal to approximately 50 ml.; this proportion of water over and above the moisture equivalent is about the maximum that can be obtained from the pressure filters or from a Buechner funnel. The volume of the extracts obtained from some of the soils in this series was as low as 20 ml., and few soils yielded more than 40 ml. The pressure filters referred to are the soil-solution displacement cylinders previously described. After transferring the soils to the cylinders they are settled into place on the filter by bringing the cylinder down sharply onto a table top a number of times.

TABLE 14.—*Boron in 1.5-moisture-equivalent extracts of 40 soils*¹

Soil No.	Boron in extractions after soil-water contact for—			Soil No.	Boron in extractions after soil-water contact for—		
	18 hours		7 days		18 hours		7 days
	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>		<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
489	0.62	0.68	0.93	511	0.47	0.49	0.97
490	.63	.70	.96	512	.75	.78	1.14
491	1.18	1.34	1.58	513	.66	.66	.73
492	1.24	1.28	1.72	514	.89	1.03	1.17
493	.95	.98	1.20	515	.85	.85	1.22
494	.91	.93	1.11	516	1.06	1.11	1.52
495	1.44	1.57	1.63	517	.66	.77	1.18
496	.55	.59	.72	518	.66	.68	.92
497	.66	.74	.83	519	.77	.81	1.12
498	.65	.79	1.04	520	.66	.80	.85
499	.57	.65	.74	521	.60	.61	.83
500	.61	.65	.87	522	.55	.61	1.09
501	.77	.85	1.15	523	1.24	1.39	1.81
502	.66	.70	1.04	524	1.02	1.02	1.46
503	.38	.41	.90	525	.67	.69	.97
504	.64	.65	.78	526	.54	.61	.83
505	1.17	1.18	1.43	527	.70	.76	1.08
506	1.13	.86	1.27	528	1.05	1.05	1.39
507	.67	.83	1.63				
508	.50	.57	1.03				
509	.69	.76	1.07	Average	.78	.84	1.13
510	.67	.72	1.09				

¹ Duplicate samples extracted after standing 18 hours and a third sample after standing 7 days. Boron determinations made by direct titration of 20 to 50 ml. of extract.

The agreements between the duplicate 18-hour extractions provide an index to the reproducibility of the method. The maximum difference between 18-hour samples was 0.16 p. p. m., and the average difference between the high and low values was 0.06 p. p. m. Eighteen hours was insufficient for complete equilibrium, as is shown by comparison with the 7-days values. The latter periods, on the basis of other work, are much longer than is necessary. It was intended that the soil-water contacts of the duplicate series would be 48 hours rather than 18 hours. The 18-hour period was employed as a result of a misunderstanding, which was not discovered until, because of the size of the samples, it was too late to start over. Eighteen hours is too short a period for a satisfactory equilibrium, but 48 hours is ordinarily ample.

SOIL-SOLUTION CONCENTRATIONS AND ASSOCIATED ACCUMULATION OF BORON IN LEMON LEAVES

To further an understanding of the effects of boron on the condition of lemon orchards of the San Fernando Valley, and at the same time provide data for correlations of soil-solution concentrations with the accumulation of boron in plants, a series of soil and leaf samples were collected from lemon orchards in the area mentioned, in the fall of 1931. The samples were taken with considerable care as regards methods and records of locations, a fact that made it possible to go back and essentially duplicate the series 5 years later in 1936. The data resulting from the collections of 1931 and 1936 are reported in table 15.

TABLE 15.—Concentrations of boron in leaves and soil ¹ solutions of 38 San Fernando lemon orchards in 1931 and 1936

Orchard group and No.	Leaf sample No.		Moisture equivalent		Grade of injury ²		Boron in soil solution		Boron in leaves	
	1931	1936	1931	1936	1931	1936	1931	1936	1931	1936
Group A: ³			Percent	Percent			P.p.m.	P.p.m.	P.p.m.	P.p.m.
1	1079	3305	17.7	17.0	7	6	1.30	0.93	732	632
2	1080	3306	15.3	14.8	4	4	1.05	.96	522	595
3	1081	3307	14.2	13.6	6	4	1.36	1.58	796	674
4	1082	3308	17.2	16.3	4	6	1.82	1.72	806	729
5	1083	3309	16.6	15.8	5	5	1.52	1.20	583	627
6	1084	3310	13.2	12.6	6	5	1.93	1.11	720	578
7	1085	3311	19.2	19.6	3	6	1.10	1.63	468	723
8	1086	3312	16.3	15.9	4	4	1.34	.72	500	472
9	1087	3313	23.7	23.3	4	4	.82	.83	538	548
10	1088	3314	25.4	25.2	4	3	1.43	1.04	558	469
11	1089	3315	22.6	22.4	5	4	.69	.74	528	532
12	1090	3316	27.0	24.7	3	4	.82	.87	542	486
13	1091	3317	18.6	17.8	2	3	.67	1.15	454	564
14	1092	3318	26.2	25.8	5	3	.73	1.04	605	442
15	1093	3319	30.0	29.3	5	4	.81	.90	520	489
16	1094	3320	26.0	25.3	4	4	.77	.78	555	475
17	1095	3321	22.0	22.4	5	4	1.20	1.43	583	489
18	1102	3327	11.3	16.1	4	5	.87	1.14	616	668
19	1103	3328	17.5	10.3	4	4	1.07	.73	643	587
20	1104	3329	14.9	19.6	4	5	.89	1.17	585	701
21	1105	3330	24.0	22.5	3	4	.81	1.22	440	486
22	1106	3331	19.1	18.4	7	7	1.39	1.52	754	666
23	1107	3332	22.9	23.6	4	4	1.21	1.18	550	513
24	1108	3333	20.7	19.8	4	7	.54	.92	526	622
25	1113	3338	11.0	10.2	8	7	1.43	1.81	894	865
26	1114	3339	15.3	14.6	7	5	.68	1.46	654	489
27	1115	3340	18.3	15.1	4	4	.80	.97	548	627
28	1116	3341	20.7	20.7	1	3	.74	.83	206	424
29	1118	3343	17.1	15.6	1	2	.58	1.39	289	363
Average					4.4	4.5	1.05	1.14	577	570
Group B: ⁴										
30	1097	3322	20.4	19.4	2	2	0.99	1.63	410	395
31	1098	3323	17.9	17.5	1	3	1.10	1.03	350	447
32	1099	3324	19.0	18.5	3	4	.70	1.07	456	461
33	1100	3325	14.2	13.4	2	2	.73	1.09	468	535
34	1101	3326	22.2	24.7	2	2	.42	.97	341	396
35	1109	3334	22.6	21.8	6	3	.96	1.12	572	456
36	1110	3335	17.6	16.4	2	2	.60	.85	248	341
37	1111	3336	13.5	12.8	1	2	.25	.83	165	387
38	1112	3337	20.6	21.8	3	3	.39	1.09	346	439
Average					2.4	2.6	.68	1.10	373	428
Average of all orchards					3.9	4.0	.96	1.12	529	537

¹ The 2 series of samples were collected from the same trees, by the same collectors, October 7, 8, and 9, 1931, and October 14 and 15, 1936.

² Scale of 10. (See text.)

³ Orchards irrigated with water from Los Angeles aqueduct.

⁴ Orchards irrigated with water from Mission wells and later partly from Los Angeles aqueduct. (See text.)

Four to six representative trees were selected in each of the orchards chosen for investigation, and from each of these trees approximately 50 leaves were taken. All leaves were picked from behind large fruits or from the second or third growth cycle from the tips, insuring ages at least between 6 and 12 months but for the most part between 7 and 9 months. The soil samples all represent the 6-to-36-inch horizon. Three cores were taken from the southwest corner of each of the trees from which leaf samples were collected. These soil samples were from the irrigated portion of the land, and the particular locations of the cores were such as to include both furrow and mid-furrow soil. The 1931 and 1936 series of samples were both collected in October by the same personnel.

The leaves were brought to the laboratory, and while they were fresh the severity of the boron symptoms was independently judged and recorded by three observers, a grade of 1 being assigned when there was no burning or yellowing and a grade of 10 to the most severely injured leaves that had been observed. The grades reported are those on which two observers agreed or the mean of three estimates. Boron determinations were made on the leaves in the customary manner, expressing the results on the basis of dry weight. Extracts by the 1.5-moisture-equivalent method were made on the entire series of soils. The results are recorded as soil-solution concentrations.

Included in this series of orchards are 29 that were irrigated exclusively with Los Angeles aqueduct water. This water contained during the years 1928 to 1931, inclusive, an average of 0.63 p. p. m. of boron and during the years 1932 to 1936, inclusive, an average of 0.77 p. p. m. of boron. There are also included in the series 9 orchards that originally were irrigated entirely with Mission well water containing 0.31 p. p. m. of boron. More recently these 9 orchards have received undetermined proportions of aqueduct water. The annual application of irrigation water on the San Fernando Valley orchards customarily varies between 20 and 24 acre-inches, and the annual average rainfall is approximately 16 inches.

The average concentrations of boron found in the soil solutions of the aqueduct-irrigated orchards in October for the years 1931 and 1936 respectively were 1.05 and 1.14 p. p. m. Making allowance for the probability that the 1.5-moisture-equivalent extracts tend to underestimate a little, it is to be noted that the average soil-solution boron concentrations were in excess of 50 percent higher than the irrigation-water concentrations. In no orchard irrigated wholly with aqueduct water was the concentration of boron in the soil solution as low as that of the irrigation water of the corresponding year; the irrigation water in 1931 averaged 0.55 p. p. m., and in 1936, 0.63 p. p. m. In other localities, soils have been observed to maintain solution concentrations substantially less than the irrigation-water concentrations for a period of years (table 16).

The general fact that the boron concentrations in the soil solutions of the different orchards of the San Fernando Valley were subject, as here shown, to much variation between 1931 and 1936 indicates on the one hand a reduction in root-zone concentrations by a more abundant use of water in some instances and, on the other, an accumulation of boron in the soil solution as a result of a slowing up in the fixation rates and of the use of insufficient water to leach from the soil quantities of boron as great as those applied.

TABLE 16.—*Boron concentrations in soil solutions of successive horizons of eight San Benito County apricot and prune orchards*

Soil type	Saturation percentage of 6- to 36-inch horizon	Period of use of the irrigation water	Boron in irrigation water	Boron in soil solution of horizon		
				0-6 inches	6-36 inches	36-72 inches
		<i>Years</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
Montezuma loam.....	57.3	9	12.5	7.94	2.63	1.33
Conejo gravelly loam.....	45.4	10+	4-16	4.63	8.31	6.85
Conejo loam.....	52.2	3	5.10	5.08	3.67	.91
Yolo silt loam.....	33.0	17	4.39	2.83	2.53	2.63
Do.....	45.5	17	.65	1.26	.93	.67
Rincon loam.....	48.1	5	1.35	1.01	1.01	.71
Conejo loam.....	52.2	11	.11	.87	1.03	2.08
Montezuma loam.....	39.1	Unirrigated62	.48	.55

¹ A number of wells have been used to irrigate this orchard. During the season preceding the sample no irrigation water was applied.

It is known that the extent of accumulation of boron in the leaves of citrus trees is in part a function of their age, and there is reason to believe that climatic conditions have a bearing on rate of uptake. The species or variety of the rootstock and scion has also been shown to be a matter of importance (14). The inorganic composition of the culture solution likewise influences somewhat boron accumulation. Notwithstanding the foregoing, differences in the concentration of boron in the soil solution can be expected to constitute the major variable determining the boron accumulation in leaves. The concentration of boron is rarely uniform, however, through the successive horizons of the root zone. In any situation it is difficult to select soil horizons for examination that most satisfactorily integrate the diversity in the vertical distribution of boron and roots. A uniform distribution of boron through the soil is rarely found (see tables 1 and 16) except where the same water supply has been in use for many years. It is well known that the feeding roots of citrus trees in some soils are largely localized in the upper 12 or 18 inches, whereas in other soils there is an extensive distribution to a depth of 5 or 6 feet.

In the present case the samples were all taken from a single valley, and as regards either year climatic conditions for all orchards were substantially the same, but as between the two years they were not wholly alike. Two varieties of lemons were grown and at least two different rootstocks were represented, but limited evidence would indicate that the boron relationships of these roots and scions are similar. As to whether the 5-year increase in age, accompanied as it was by evidence of loss of vigor in some orchards, was a significant factor is uncertain. The samples were taken during the irrigation season before the winter rains, and in both seasons there was marked variability in the moisture content of the soils at sampling time. The recent new growth was not in the same stages of advancement in all orchards, and as between the years 1931 and 1936 there may have been important differences in the ages of the leaves sampled as a result of complex factors affecting the time at which the growth cycle chiefly represented appeared. Four principal soil series were represented, and of each of these soil series there were a number of types. The texture varied from that represented by a moisture equivalent of 10.3 to that represented by 30.0. All of these factors, in addition to

those related to management, have doubtless affected the relationships between boron concentrations found in the lemon leaves with those of the soil solutions (fig. 4).

The data of the 1931 series are represented in figure 4 by solid points and those of 1936 by open circles. The points of corresponding orchards for the two years are connected by lightly traced lines. The correlation coefficients, r , between boron in leaves and boron in soil solutions for the separate years and for the two years considered as one array are as follows:

$$\begin{aligned} 1931, r &= 0.74 \pm 0.050 \\ 1936, r &= 0.41 \pm 0.091 \\ 1931 \text{ and } 1936, r &= 0.59 \pm 0.050 \end{aligned}$$

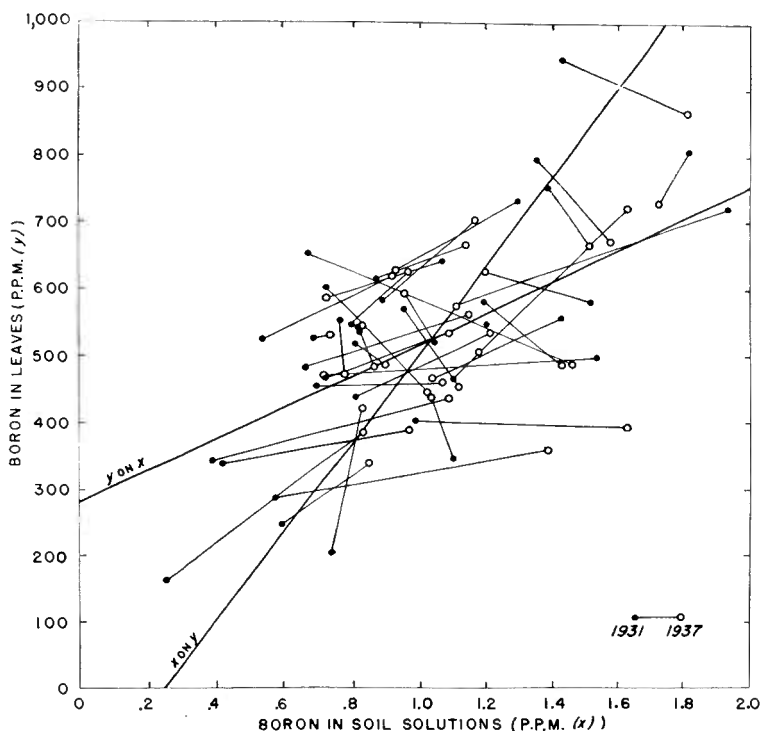


FIGURE 4.—Boron in leaves (y) and in soils (x) in 38 lemon orchards in the San Fernando Valley, Calif., in 1931 and 1936.

Boron in leaves, since it is a function of boron of the soil, has been taken as the y coordinate and the boron in the soil as the x coordinate. The equation of the straight lines through these points (y on x and x on y), as derived by the method of least squares for the combined years and the corresponding standard errors (root mean square error), are as follows:

$$\begin{aligned} \text{Regression of } y \text{ on } x: \quad y &= 284.6 + 238.2 x \\ Sy &= 112.9 \text{ p. p. m.} \end{aligned}$$

$$\begin{aligned} \text{Regression of } x \text{ on } y: \quad x &= 0.243 + 0.0015 y \\ Sx &= 0.28 \text{ p. p. m.} \end{aligned}$$

The equations for the two regressions were calculated also from the correlation coefficients with the same results.

Though it is not the purpose of this bulletin to discuss physiological aspects of the boron problem, prior considerations as well as the appearance of these data had prompted the view that the line of best fit for y on x would more nearly pass through the origin than is found to be the case. It was not expected, however, that a straight-line function would fit the data very well at either extremity. This would be the case, since, with no boron in the soil, there could be little or none in the plant. A solution concentration of 0.1 p. p. m. in controlled experiments has resulted in proportionately greater accumulation than that from solution concentrations of 1 p. p. m. A straight-line relationship between the intermediate and high concentrations would presuppose that boron continues to accumulate with time in injured leaves at the same rate that it accumulates in uninjured leaves. This is not the case. Boron accumulates at the margins of leaves more than in the midareas and in the veins (12). As excessive concentrations develop in the margins, these margins yellow and die, with the result that the boron input into a leaf steadily diminishes after burning has started. In other words, the concentration that kills the margin of a leaf constitutes a maximum value. Yellowing precedes burning, and a question exists as to how functional the yellow areas are. The fact that so many of the points represented in these data are grouped in the midrange tends to emphasize considerations in that zone. Through this zone a straight-line relationship is believed to fit the data on the basis of results from sand-culture experiments reported elsewhere (12).

The measurement of boron in soils should on theoretical grounds constitute a more basic measurement than boron in leaves. This is particularly the case since in some plants, the stone fruits for example in contrast to citrus and others, considerable translocation of boron from one organ to another occurs. As applied to citrus, nevertheless, accumulation in leaves is a more satisfactory index to boron conditions than soil measurements. Because of the uncertainty that accompanies the selection of soil horizons most representative of root distribution, leaf analyses are more extensively used than soil analyses. For these reasons the y -on- x regression is the more useful relationship.

BORON FIXATION IN RELATION TO SOIL TEXTURE

Some indication has been afforded by the evidence of injury in field plantings that heavy soils tend to fix more boron than do light soils. Several of the preceding tables provide confirmatory suggestions. If it be assumed, as is probably justified, that boron concentrations found in the soil solutions of a series of plantings such as the aqueduct-irrigated orchards of the San Fernando Valley reflect inversely though not necessarily proportionally the amount of fixation that has occurred, then a fairly direct examination of the relation between texture and fixation is possible.

Recalling that each of the San Fernando samples was a composite of the soil between 6 and 36 inches, and also that to a variable degree decreasing concentrations of boron probably occurred with depth, it seems evident that some redistribution and fixation of boron took place between soil particles when these composite samples were

screened, mixed, rewetted, and packed in the laboratory. High-boron particles would be brought in contact with low-boron particles, with opportunity for boron released by the former to be removed from solution by the latter. This redistribution might conceivably result in a solution concentration of the mixed sample that would be lower than the averages of the solution concentrations of several horizons had they been taken separately. Leaching beyond the root zone as a result of rains and irrigation would favor a greater loss of boron in the field from the light soils than from the heavy soils.

The soil-solution data for 1931 and 1936 from the 29 orchards irrigated with aqueduct water (table 15), when classified into 5 groups on the basis of moisture equivalent (table 17), show an inverse relationship between the moisture equivalent and the concentration of boron in the soil solution. This stated otherwise means that a greater fixation had taken place in the finer-textured soils. The concentration of boron in leaves, other than for the final value, also decreases as the moisture equivalent increases.

The coefficient of correlation between the moisture equivalent and boron in the soil solutions for the 58 pairs of values is—

$$r = -0.35 \pm 0.078$$

This coefficient of correlation is clearly significant, but its magnitude is such as to show that soil characteristics other than texture have influenced fixation. Rough computations indicate that the relative surfaces of soils with moisture equivalents of 10, 20, and 30 would be in the general ratio of 10 to 30 to 45.

The effect of grinding on the boron-fixing power of soils and kaolinite will be dealt with in a later section of this bulletin.

TABLE 17.—*Relation between soil texture and boron concentrations in soil solutions and in lemon leaves*

Moisture-equivalent range	Orchards	Boron in soil solution	Boron in leaves	Moisture-equivalent range	Orchards	Boron in soil solution	Boron in leaves
	<i>Number</i>	<i>P. p. m.</i>	<i>P. p. m.</i>		<i>Number</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
10 to 13.9	7	1.35	705	22 to 25.9	15	1.02	509
14 to 17.9	20	1.16	594	26 to 30.0	5	.81	543
18 to 21.9	11	1.03	558				

BORON FIXATION BY MATERIALS OTHER THAN SOILS

BORON FIXATION BY AN ARTIFICIAL ZEOLITE

An artificial zeolite, sold under the trade name Duocil, has been studied as regards its boron-fixing power. The formula supplied with this material was $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ plus 50 percent of water. On working with the zeolite it was found that in addition to other possible impurities it contained a substantial quantity of boron. In appearance the material was homogenous and uniform. The individual particles, approximately 2 mm. thick, were nearly transparent, but on exposure to the air they dried to an amorphous white.

A series of 1-to-1 suspensions of Duocil was prepared in which sodium tetraborate solutions were used as the aqueous phase in concentrations of 0.0, 0.0005, 0.005, 0.02, and 0.1 normal. These suspensions were allowed to stand with recurrent shaking for a 7-day

period before filtration. The Duocil obtained 43.8 percent of moisture on the basis of its weight as used. The results are shown in table 18.

TABLE 18.—*Adsorption of boron by an artificial zeolite (Duocil) in 1-to-1 suspensions with sodium tetraborate*

Na ₂ B ₄ O ₇ as weighed to make up initial solution		Boron found at end of test in—		Adsorption	Na ₂ B ₄ O ₇ as weighed to make up initial solution		Boron found at end of test in—		Adsorption
Normality	Boron	Solutions without Duocil	1:1 suspensions with Duocil		Normality	Boron	Solutions without Duocil	1:1 suspensions with Duocil	
	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>Percent</i>		<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>Percent</i>
0	0	0	27	0	0.02	433	448	182	59
.0005	11	11	32	0	.1	2,164	2,247	874	61
.005	108	112	67	40					

Duocil fixed 0.14 percent of its weight of boron, corresponding to 1.2 percent of borax, when suspended in 0.1-normal sodium tetraborate. No aluminum was found in any of the filtrates. Silica was present in the 0.0 suspensions to the extent of 118 p. p. m. and in the 0.1-normal sodium tetraborate suspension to the extent of 76 p. p. m. Referenced to 100 gm. of Duocil, there was fixed in the 0.1-normal suspension 37.8 mg. equivalents of boron, and silica was released to solution to the extent of 0.50 mg. equivalents.

If boron was fixed by this material as a result of an exchange reaction with aluminum, the aluminum released was at once precipitated as aluminum hydroxide. There being a possibility that replaced aluminum would remain dissolved in more acid solutions, a 1-to-1 suspension of Duocil in 0.02-normal hydrochloric acid was prepared. This suspension, which was neutral to methyl orange, pH about 4.5, was found to be rich in aluminum before boron was added, which of course eliminated the possibility of further progress in this direction. The addition of stronger acid brought more aluminum into solution. This avenue of approach apparently being closed, final suspensions were prepared with 0.1-normal sodium carbonate containing 0.1-normal borax. It was thought that the aluminum might remain in solution as sodium aluminate. Tests for aluminum were negative.

The fixation of boron by Duocil is discussed further at the end of the next section, which deals with magnetite.

BORON FIXATION BY MAGNETITE

As a byproduct of an investigation (13) of the availability to plants of the iron of magnetite, FeO·Fe₂O₃, some evidence resulted that this material, when freshly used, removes measurable amounts of boron from culture solutions. Cotton plants, the boron requirements of which are relatively high (11), were grown in each of two Oldberg-type percolators containing 2 kg. of acid-washed quartz sand. Four grams of finely ground magnetite was mixed with the sand in one of the cultures. The other culture was without magnetite. The nutrient solution supplied to each of the cultures was from the same stock. It contained 1.0 p. p. m. of boron. When the plants were about 40 cm. high and while the fourth change of nutrient solution was in use, boron-deficiency symptoms were observed on the cotton in the magnetite

jar. The control cotton did not exhibit deficiency symptoms. It was found upon analysis that the solution in use on the magnetite culture contained 0.01 p. p. m. and that on the control culture 0.28 p. p. m. of boron. The deficiency symptoms of the magnetite cotton became more severe with time, but none were developed by the control cotton.

With the foregoing observations as a background, the boron adsorption of magnetite was measured in an experiment that paralleled the experiment with the zeolite reported in the preceding section. The two experiments were conducted at the same time. The results are presented in table 19.

TABLE 19.—*Adsorption of boron by powdered magnetite in 1-to-1 suspensions with sodium tetraborate*

Na ₂ B ₄ O ₇ as weighed to make up initial solutions		Boron found at end of test in—		Adsorption	Na ₂ B ₄ O ₇ as weighed to make up initial solutions		Boron found at end of test in—		Adsorption
Normality	Boron	Solutions without magnetite	1:1 suspension with magnetite		Normality	Boron	Solutions without magnetite	1:1 suspension with magnetite	
	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>Percent</i>		<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>Percent</i>
0	0.0	0.0	0.3	0	0.02	433.0	448.0	370.0	17
.0005	10.8	11.2	8.2	27	.1	2,164.0	2,247.0	1,807.0	20
.005	108.0	112.0	92.0	18					

The magnetite removed 17 percent or more of the boron from each of a series of 1-to-1 suspensions, the sodium borate solution concentrations of which ranged from 0.0005 to 0.1 normal, the latter containing 2,247 p. p. m. of elemental boron. The magnetite used had been ground to an impalpable powder, and the surfaces exposed were accordingly great. Questions of some interest were presented by these results and a further experiment was made. In this second series of measurements (table 20), boric acid, sodium tetraborate, and sodium tetraborate plus sodium hydroxide were used to permit of observations on the effect of hydrogen-ion concentration on fixation.

TABLE 20.—*Fixation of boron by magnetite in 1-to-1 suspensions*

Item	H ₂ O	H ₃ BO ₃	Na ₂ B ₄ O ₇	Na ₂ B ₄ O ₇ + NaOH
Original solutions:				
pH	6.2	5.5	9.2	-----
K $\times 10^6$.3	.5	78.7	-----
Na	-----	.48	10.62	91.00
B	-----	19.78	20.14	42.14
Filtrate from suspensions:				
pH	4.5	4.3	5.5	8.9
K $\times 10^6$	266.0	264.0	291.0	512.0
Na	7.70	7.58	16.73	57.23
B	-----	17.38	16.36	27.36
Fixation:				
B	-----	12.7	18.7	35.3
	percent			

It was found that the substitution of sodium tetraborate for boric acid raised the pH value of the suspensions from 4.3 to 5.5 and increased boron fixation from 12.7 percent to 18.7 percent (table 20). The addition of sodium hydroxide increased the pH value of a sodium borate suspension of magnetite to 8.9 and increased boron fixation to 35.3

percent. At this concentration the boron fixation by magnetite was one-half as great as that experienced with Duocil at a similar pH value. The magnetite as here shown contained soluble sodium as an impurity, and there were other constituents as well, since the electrical conductance of the distilled water suspension was 266×10^{-5} , indicating a concentration of all bases of about 30 mg. equivalents per liter.

There are a number of borate minerals containing iron. In connection with the description of one of them, vonsenite, $2(\text{FeMg})\text{O} \cdot \text{B}_2\text{O}_3 + \text{FeO} \cdot \text{Fe}_2\text{O}_3$, Eakle (10) has suggested a derivation by the action of borate solutions on magnetite. He did not suggest the conditions that might be required for the reaction.

The boron-fixation characteristics of both Duocil and magnetite appear to stand in contrast to the fixation characteristics of soils as brought out in figure 2. The percentage of the boron added to soils that was fixed decreased as the concentration of solution was made greater. There is no evidence of this effect with either Duocil or magnetite, and the point would seem to be quite an important one. The writers believe, however, that the apparent distinction can be attributed to changes in pH value associated with the introduction of sodium tetraborate. Through an oversight, no pH measurements were made on the original magnetite suspension (table 19). The data of table 20 show, nevertheless, that the magnetite in distilled water had a pH value of 4.5 and in 0.01-normal sodium tetraborate of 5.5; presumably the pH value of the 0.1-normal sodium tetraborate suspension was substantially higher. These increases in pH value, as shown by table 20, would be accompanied by an increased fixation of boron, by offsetting, in some measure at least, the decrease in percentage of fixation that was shown by the soils to accompany increases in concentration. Information on the hydrogen-ion concentration of the Duocil suspensions is limited to the three higher concentrations, which suspensions had been set aside in the laboratory after the others were discarded. The 0.005-, 0.02-, and 0.1-normal sodium tetraborate suspensions had pH values of 9.7, 9.6, and 9.2, respectively. Boron fixation by Duocil (table 18) tended to increase on the percentage basis over this high pH range, which is in accord with the behavior of two of the four soils shown in figure 3. In other words, it seems not unlikely that the behavior of Duocil and magnetite as regards the effect of hydrogen-ion concentration and increasing concentrations on boron fixation is in line with the behavior of soils.

BORON FIXATION BY BENTONITE

The boron-fixing power of two samples of bentonite has been measured. One of these, from Ardmore, S. Dak., was so highly dispersed that much difficulty was experienced in filtering off enough solution for analysis from other than very dilute suspensions. The second bentonite, designated montmorillonite, was supplied by A. P. Vanselow from a lot secured in San Diego County, Calif. This latter has the formula—



The several boron solutions used in the experiment were prepared with boric acid and all contained 10 millimoles per liter of calcium sulfate. Boric acid solutions of each concentration were stored without bentonite as a check against changes attributable to the effects of

the glassware. The initial concentrations of the check solutions were very close to those desired, and there was little subsequent change, but minor corrections have been applied. The suspensions were agitated frequently during the initial 3-day period and once a week or so during the 5-month period, but they were almost wholly neglected during the subsequent portion of the 45-month period.

The effect of heating on boron fixation was measured in a duplicate of the 5-p. p. m. bentonite suspension. This suspension was boiled under a reflux condenser for 40 hours at the beginning of the experiment.

The Ardmore bentonite (table 21) even in these dilute suspensions removed relatively large amounts of boron from all solutions. The solution concentrations of the 1-to-30 suspensions were reduced by as much as 25 to 50 percent on long standing. In the 3-day period boron was fixed from a 10 p. p. m. solution to the extent of 45.3 mg. per kilogram, or 0.44 mg. atoms of borax per 100 g. The Ardmore bentonite presumably carried a substantial amount of adsorbed sodium, since on washing it with a sodium salt its degree of dispersion was unchanged, but upon washing it with a calcium salt it was flocculated. Its dispersion, however, was not affected very much when suspended in the 10 millimolar calcium sulfate solution. The montmorillonite was not dispersed. The filtrate from a 1-to-1 suspension of the Ardmore bentonite had a pH value of 9.1, and that from the montmorillonite was 8.1. The boron fixation by this latter material was only about one-seventh that of the Ardmore bentonite. Heating the suspension of Ardmore bentonite materially reduced boron fixation.

TABLE 21.—*Fixation of boron by bentonite from Ardmore, S. Dak., and montmorillonite (bentonite) from San Diego, Calif.*

Designation	Initial boron concentration	Ratio of material to solution	Concentration of boron in solution after—			Boron fixed per kilogram of material		
			3 days	5 months	45 months	3 days	5 months	45 months
	<i>P. p. m.</i>		<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>Mg.</i>	<i>Mg.</i>	<i>Mg.</i>
Bentonite	0	1 to 30	0	0.02	0	0	0	0
	1		.68	.54	.38	8.4	12.9	17.7
	3		2.37	2.15	1.89	16.5	26.4	36.3
	5		4.22	3.86	2.62	20.7	34.8	68.7
	10		4.56	4.22	3.73	10.5	24.0	42.0
Montmorillonite	10	{--do-- 1 to 5	8.49	8.44	7.70	45.3	48.3	68.4
			9.77	9.89	9.32	6.3	2.7	19.8
	10		8.70	7.77	-----	6.4	11.0	-----

¹ Heated under reflux.

A comparison of these results with those of table 4 shows the Ardmore bentonite to have fixed substantially more boron than any of the six soils there represented. The fixation by montmorillonite was of the same order as the soils.

BORON FIXATION BY ORGANIC MATTER

The activity of the organic matter of the soil with respect to boron fixation has received little attention. The possibilities of a substantial fixation have not been regarded as very great, but in this conclusion the writers may be in error. The alkali-soluble fraction of peat after acid precipitation and washing did not remove a measurable amount

of boron when suspended for 48 hours in 1-p. p. m. solution of boron made up with boric acid. Similarly, there has been no indication that boron is fixed by cellulose material such as filter papers. In line with a discussion in another paper (13) boron does react with organic substances such as glycerol and certain polyhydric alcohols, but the resulting compounds are soluble. Plants growing on soils high in water-soluble boron sometimes accumulate 1,000 p. p. m. or more of boron in their leaves. From 50 to 100 percent of this boron has been found to be in solution in the expressed plant sap after freezing. The boron of plant material is for the most part readily soluble in water. Essentially as much boron may be removed from dried and ground plant material by repeated leaching with water as can be obtained by distillation with methyl alcohol.

FIXATION OF BORON IN THE FORM OF CALCIUM BOROSILICATE

A demonstration that it is possible to precipitate boron in the form of highly insoluble borosilicates from solutions of electrolytes such as are found in soils and under conditions that might exist in soils would go far in the way of a suggestion on the mechanisms of boron fixation. Silica in concentrations of 10 p. p. m. or more is a normal constituent both of soil solutions and irrigation waters, and calcium, as well as other bases, is invariably present. Desiccation is conducive to the irreversible precipitation of silicon compounds. That boron compounds with or without silica should be precipitated in soils is more to be expected than otherwise; but it does not follow that borosilicate compounds formed under field conditions would be very insoluble. Rather than to pass this subject by wholly on a speculative basis, several minor tests were conducted. These are not regarded as being either exhaustive or conclusive.

The proportions of boric acid, calcium oxide, and sodium silicate required for a borosilicate corresponding to bakerite, $8\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 6\text{SiO}_2$, were mixed at room temperatures by adding the compounds in the order named to distilled water in amounts sufficient to produce a 5-percent solution or suspension. After stirring mechanically for 1 day, the mixture was allowed to stand for several days, the precipitate then being filtered off, washed with water, and resuspended in 2 liters of water. After three successive washings by suspension and filtration the precipitate remaining was roughly one-third of the theoretical. Five grams of the dried precipitate when added to 1 liter of water gave rise to concentrations of boron in solution as follows:

	<i>P. p. m.</i>
1 hour.....	3. 23
2 hours.....	4. 10
15 hours.....	15. 7
18 hours.....	55. 4

It is obvious that a boron compound of this character in a soil would be regarded as a soluble rather than an insoluble one.

As a continuation of the calcium borosilicate inquiry, measurements were made of boron fixation by a freshly prepared calcium silicate. The calcium silicate was obtained by slowly adding sodium silicate to limewater. Suspensions of 0.5 gm. of calcium silicate per 100 ml. of water when added to 1-liter portions of 5- and 25-p. p. m. boron solutions prepared with boric acid in distilled water had the effect shown in table 22.

TABLE 22.—*Fixation of boron by suspensions of calcium silicate*

Time	Concentration of boron found in solution				Time	Concentration of horon found in solution			
	1 liter 5-p. p. m. boron solution diluted with—		1 liter 25-p. p. m. boron solution diluted with—			1 liter 5-p. p. m. boron solution diluted with—		1 liter 25-p. p. m. boron solution diluted with—	
	100 ml. calcium silicate suspension	100 ml. distilled water	100 ml. calcium silicate suspension	100 ml. distilled water		100 ml. calcium silicate suspension	100 ml. distilled water	100 ml. calcium silicate suspension	100 ml. distilled water
20 minutes	<i>P. p. m.</i> 3.42	<i>P. p. m.</i> 4.43	<i>P. p. m.</i> 18.30	<i>P. p. m.</i> 22.88	5 hours	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i> 18.09	<i>P. p. m.</i>
2 hours	3.52	4.50	18.36	22.79	24 hours			18.67	

An interpretation of the results of the experiment presented on page 44 in the light of those presented in table 22 is not at once evident. The boron of a suspension of 5 gm. per liter of a material thought to be a calcium borosilicate was soluble to the extent of 55 p. p. m. or more, whereas a suspension of 0.5 gm. per 1,100 ml. of a similarly prepared calcium silicate without boron reduced the concentrations of both 5- and 25-p. p. m. boron solutions by approximately 20 percent.

AVAILABILITY TO PLANTS OF BORON IN A TOURMALINE-QUARTZ MINERAL

Because of the occurrence of tourmaline in some soils, a more than passing interest is associated with the question of the availability of its boron to plants. This question has recently been discussed by Dennis and O'Brien (9), who associated the prevalence of brown heart of turnips with the absence of tourmaline crystals in certain Scottish soils examined by Elder and McCall (15). The former clearly doubted the availability of boron of tourmaline but thought nevertheless that the presence of tourmaline argued the presence of other boron compounds in the parent rocks from which the soils were derived.

A demonstration that deficiency symptoms result when plants are grown on a substrate consisting principally of finely divided tourmaline would constitute evidence that the boron was not available irrespective of extraneous impurities. If, on the other hand, plant growth was adequately supported, evidence of availability as regards boron of tourmaline would be demonstrated only in the event that clean tourmaline crystals had been selected and pulverized for use as the substrate.

A tourmaline-rich quartz from a vein opened by the American Tin Co. at the Cajalco tin mine near Riverside, Calif., was available for study. Tomatoes and cotton plants were grown in each of three cultures. Oldberg-type percolator tubes were used as vessels. In each of these, 2 kg. of the material to be tested was placed above a wad of glass wool to provide free drainage. Each culture was supported by a nutrient prepared from recrystallized chemicals. Acid-washed quartz sand was used in the culture designated *a* (pl. 1).

Culture *b* was tailings from a Wilfrey concentration table of the testing plant. These tailings had lain on top of the dump exposed to the atmosphere and rain from 1928 to 1937. Though ground to pass a 60-mesh screen, some of the material was much finer. By fusion analysis the tailings contained 1.17 percent of boron. There was a substantial proportion of quartz in this material. Culture *c* was freshly ground selected specimens of heavy black rock with only a few quartz inclusions, taken at a depth of 780 feet from a vein outcropping on the surface. This preparation, which contained 1.45 percent of boron by fusion analysis, was more finely ground than the preceding, much of it passing a 200-mesh screen.

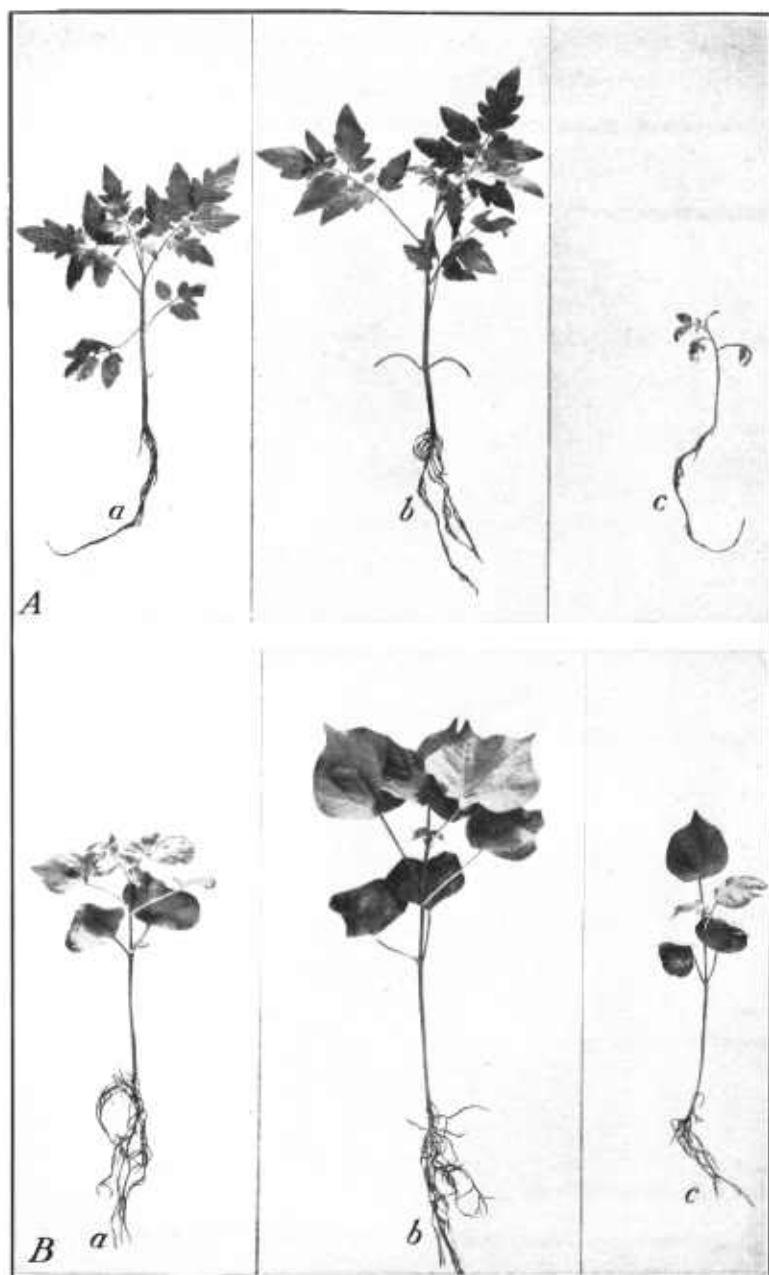
The plants in the quartz sand (*a*) developed marked boron-deficiency symptoms; those in the tailings (*b*) were vigorous and wholly normal in appearance; those in the tourmaline-rich quartz (*c*) were severely injured. The 1.5 liters of nutrient solution used for each culture was passed through the percolators a number of times each week during the growth of the plants, transpiration loss being made up with distilled water. At the end of 4 weeks aliquots were taken of the three nutrient solutions for boron analyses, with the following results: *a*, Quartz sand, less than 0.01 p. p. m.; *b*, tailings, 0.1 p. p. m.; *c*, ground specimens, 12.7 p. p. m.

It would be in no way reasonable to suppose that all of the boron in the original intrusive material could have crystallized out in the form of tourmaline during cooling, leaving no boron in the less refractory matrixes in which the crystals grew. It is concluded that the boron that came into solutions was from the matrixes rather than from the tourmaline itself. The pulverized material as observed under the microscope was rich in well-defined purple tourmaline, but there was also other silicious material in addition to the quartz.

EFFECT OF GRINDING SOIL AND KAOLIN ON BORON FIXATION AND EXCHANGE REACTIONS

In a preceding section it was shown that the finer-textured soils of the aqueduct-irrigated groves of the San Fernando Valley had fixed more boron than had coarse-textured soils. In this section the relation of surface to boron-fixing power is subjected to a more direct examination; comparisons are made between ground and unground soil, kaolinite, and quartz sand.

The soil used in these measurements was No. 242 shown in figure 2. The first of the two kaolinite samples was supplied by W. P. Kelley, of the University of California, from a lot that had been ground dry for 12 days in a rubber-lined mill with agate balls. The second kaolinite (labeled kaolin) was from a chemical supply company, and it, like the soil and the quartz sand, was ground in an ordinary mill with glass balls. When ground wet, a 1-to-5 suspension with 0.2-normal sodium tetraborate was employed, the suspensions being filtered at the end of the grinding period. When unground and when ground dry the materials were held with frequent shaking for 48 hours in a 1-to-5 suspension of 0.2-normal borate solution before filtration. Fixation was determined by difference on the basis of the change in the concentration of boron in the initial and filtered solutions. No measurements were made of the fineness of grinding, but the results indicate that wet grinding was more effective than dry grinding.



Tomato (A) and cotton (B) plants grown to test availability of boron in tourmaline-quartz mineral from tin mine: *a*, Quartz sand as control; boron in solution less than 0.01 p. p. m. *b*, Tailings from dump after weathering 9 years; boron in solution, 0.10 p. p. m. *c*, Freshly powdered specimens selected for weight and appearance of uniformity; boron in solution, 12.7 p. p. m.

Cation exchange capacity was measured on similarly treated materials by the neutral NH_4 -acetate method. It has already been shown that boron fixation increases as the pH value of the suspension is raised from 5.5 to a value of 9.0 or more. The first of the two kaolinites became more acid with grinding, and the 0.2-normal sodium tetraborate used in a proportion of 5 parts of solution to 1 of soil was insufficient to restore the hydrogen-ion concentration of the suspension to that of the unground material; pH measurements were not made on the ammonium acetate suspensions. As distinct from the rapidity of base exchange reactions, boron equilibria are only slowly established, and sufficient time may not have been allowed for the establishment of final equilibrium in all of these suspensions.

Grinding increased the base-exchange capacity (table 23) of both the soil and the kaolinite, in keeping with the findings of Kelley and Jenny (19), and likewise of the quartz sand. Boron fixation was likewise increased by grinding. Though the increases in boron fixation and in cation exchange capacity tend to be in the same order of magnitude, equivalent increases in the adsorption capacity of the materials for the B_4O_7 and NH_4 ions is not indicated.

TABLE 23.—*Effect of grinding on fixation of boron by soil, kaolinite, and quartz sand*

Material	Treatment	pH of horax sus- pension	Fixation of boron		Cation exchange capacity	
			B_4O_7 per 100 gm.	Ratio to unground material	Per 100 gm.	Ratio to unground material
			<i>Mg. equiv.</i>		<i>Mg. equiv.</i>	
Soil 242	Unground.....	9.2	3.1		11.4	
	Ground dry, 86 hours ..	8.8	4.6	1.5	18.8	1.6
	Ground wet, 24 hours ..		8.6	2.8		
	Ground wet, 48 hours ..	9.2	10.3	3.3	90.3	7.9
Kaolinite	100-mesh ..	8.7	3.2		8.0	
	Ground dry, 12 days ..	7.3	17.2	5.4	67.0	8.4
	Unground.....	9.0	3.1		2.8	
Kaolinite 2	Ground wet, 90 hours ..	8.9	13.0	4.2		
	Ground wet, 24 hours ..				14.9	5.3
	80-200 mesh ..	9.1			.2	
Quartz sand	Ground wet, 48 hours ..	9.5	4.7		40.8	204.0

The breaking of bonds of the crystal lattices of minerals by grinding must unavoidably result in equivalent numbers of unsatisfied negative and positive valences. These valences would be available for binding cations and anions respectively. In the case of kaolinite, both H^+ and OH^- ions are exposed, and these, according to position, are generally assumed to be subject to replacement by other bases and anions. The extent to which they are replaced, however, by a particular introduced ion invites other questions such as replacement energies and the concentrations of the introduced ions as well as of the ionizable constituents of the materials.

DISPLACEMENT OF BORON FROM SOIL BY PHOSPHATE, OXALATE, AND OTHER ANIONS

The results of such direct investigations as were made on the subject of boron displacement by anion exchange are presented in table 24. The inquiry had as its purpose the establishment of some criteria as

to the extent to which (1) boron fixed by a soil is more effectively displaced by 0.2-normal solutions of a series of sodium salts than by water, and (2) the relative replacement energies of the selected anions.

TABLE 24.—Displacement of boron from finely ground soil 242 by phosphate, oxalate, and other anions

Salt added ¹	pH of suspensions	Humate (light transmission of filtrate)	Recovery of anion added	Boron per 100 gm. soil
		<i>Ohms</i> ²	<i>Percent</i>	<i>Mg. equiv.</i>
Sodium aluminate, NaAlO ₂	8.9	915	0	3.1
Sodium chromate, Na ₂ CrO ₄	8.9		104	3.9
Sodium silicate, Na ₂ SiO ₃	9.0	435	2	4.0
Sodium acetate, NaC ₂ H ₃ O ₂	8.8	850	104	4.3
Water (duplicate tubes).....	9.0	740		4.4
	9.0	750		4.3
Sodium chloride, NaCl.....	8.8	860	99	4.4
Sodium thiosulfate, Na ₂ S ₂ O ₃	8.8	890	98	4.6
Sodium carbonate, Na ₂ CO ₃	9.0	445	³ 31	4.7
Sodium nitrate, NaNO ₃	8.8	840	100	4.7
Sodium bromide, NaBr.....	8.8	915	102	4.8
Sodium sulfate, NaSO ₄	8.8	810	107	4.8
Disodium phosphate, Na ₂ HPO ₄	8.9	745	75	5.2
Sodium citrate, Na ₃ C ₆ H ₅ O ₇	8.9	188	100	5.4
Sodium oxalate, Na ₂ C ₂ O ₄	8.8	165	76	5.6

¹ 1-to-20 suspensions with 400 mg. equivalents of the salt per 100 gm. of soil.

² Photoelectric colorimetric readings. Distilled water gave a reading of 960 ohms resistance.

³ An additional 25 percent was present as bicarbonate.

Soil 242 was ground in the ball mill to increase its boron-fixation capacity and to produce particles of such fineness that the resulting suspension would be relatively stable, thus permitting the withdrawal of equal suspension aliquots without intermediate drying between the treatment with sodium tetraborate and with the series of electrolytes.

A 100-gm. portion of the soil was placed in a porcelain mill with 500 ml. of 0.2-normal sodium tetraborate solution and ground for 24 hours. The resulting suspension was then filtered on a Buechner funnel and the boron in the filtrate determined. The soil on the Buechner was washed with 100 ml. of water and the filtrate combined with washings from the mill, flasks, etc. The quantity of boron in the combined filtrate was determined. The soil, while still on the Buechner funnel, was washed a second time with 100 ml. of water and the boron in the filtrate determined.

On the basis of the volume and boron concentration of the initial 500 ml. of 0.2-normal sodium tetraborate solution and the volumes and boron content of the three filtrates, the soil retained 86 mg. of boron per 100 gm. This quantity of boron is equivalent to 23.8 mg.-equivalents of boron, or to 3.91 mg.-equivalents of B₄O₇⁻⁻⁻. By analysis, there was 2,198 mg. of boron in the initial solution, and the successive filtrates contained respectively 1,630, 425, and 57 mg.

The moist soil was resuspended in a quantity of water such that 25 gm. of the suspension would contain 5 gm. of soil on the dry basis. This suspension was mixed in the ball mill for 1 hour to insure complete dispersion of all aggregates formed while on the Buechner funnel. To 25-gm. aliquots of this suspension, 20 ml. of normal solutions of the sodium salts were added, after which they were adjusted to pH 9.0 with hydrochloric acid and sodium hydroxide, the pH measurements being made with a glass electrode. A pair of duplicate

suspensions were carried through in water to which hydrochloric acid or sodium hydroxide was added. The total weight of each suspension was then adjusted to 105 gm., i. e., 5 gm. of soil in 100 gm. of 0.2-normal solution. On the third day the pH value of each was again checked and adjusted as necessary, and again on the eighth day. The samples were reweighed on the tenth day, the final pH measurements having been made the previous day. Boron was determined in the filtrates with corrections for volume changes where filtration was slow. The recovery of boron added to pure solutions of the salts used in this experiment was in all cases satisfactory.

Prolonged standing in water at pH 9.0 liberated 4.35 mg.-equivalents or 18.3 percent of the 23.8 mg.-equivalents of boron held by this finely ground soil. When suspended in sodium aluminate, chromate, and silicate, 4.0 mg.-equivalents or less of this boron was released to the solution. In solutions of sodium phosphate, citrate, and oxalate in excess of 5.0 mg.-equivalents of boron was liberated. The actions of sodium acetate, chloride, nitrate, carbonate, bromide, and sulfate were, like water, intermediate in their effectiveness. In the more salient features, these results are not very unlike those of Demolon (7) and Demolon and Bastisse (8), who found at pH 6.6 that phosphate was displaced from soil colloids more effectively by potassium tartrate, silicate, oxalate, and citrate (in the ascending order) than by water, and less effectively by potassium bicarbonate, acetate, nitrate, sulfate, and chloride (in descending order). About one-third of the phosphate in Demolon's original material was brought into solution by water alone.

It is probable, if not certain, that in some measure anion exchange is represented by the results here presented, but to what extent the writers are unable to conclude. If anion exchange was in fact the primary reaction, important questions are at once presented. It seems notable that water alone should have been more effective than a number of the anions. The most effective anions, such as phosphate, citrate, and oxalate, liberated only a little more boron than did water.

The concentrations of the introduced anions were measured in aliquots of the filtrates by standard methods, but the concentrations in the initial solutions were not determined by analysis. It is not intended, accordingly, that the results setting forth the recovery of the added anions should be interpreted in terms of stoichiometric exchange; the main concern here was the extent of precipitation of such ions as aluminate, silicate, and phosphate. A 25-ml. aliquot of the final borax-treated suspension yielded 15.5 mg.-equivalents of calcium per 100 g. of soil when filtered after the addition of sufficient hydrochloric acid to bring the suspension to pH 4.0. The loss of 96 mg.-equivalents of oxalate per 100 gm. of soil cannot be accounted for as calcium oxalate precipitation. Solubility data suggest that calcium phosphate is at least as soluble as calcium carbonate at pH 9.0.

An observation aside from the original purpose of this inquiry was made on the displacement of humate. The citrate and oxalate ions, which most effectively displaced boron, brought relatively large quantities of humate into solution. The filtrates from these suspensions were very dark (fig. 5). Silicate and carbonate, which had only nominal effects on boron displacement, were next in line. Aluminate, which reduced boron solubility to a minimum, likewise gave a solution essentially free from humus. The concentrations of humus brought

into solution are reflected by the light transmission measurements reported in table 24. The color of the final water extractions as reported in table 24 was not very different from those of the filtrates that had preceded.

Mattson (21) has observed that on treatment of a soil with aluminum hydroxide, the aluminum is precipitated and becomes strongly associated with the complex, increasing the isoelectric pH value and decreasing the cation exchange capacity. Treatment with strong bases increased the cation-exchange capacity. Treatment with silicate and phosphate lowered the isoelectric pH value, increased cation exchange, and reduced, theoretically at least, the anion exchange capacity. According to Mattson, these latter ions, like aluminum, are strongly associated and are themselves not easily displaced.

The results here presented on the subject of boron replacement by anion exchange are regarded as being rather inconclusive. It is possible and perhaps wholly probable that substitution reactions play an

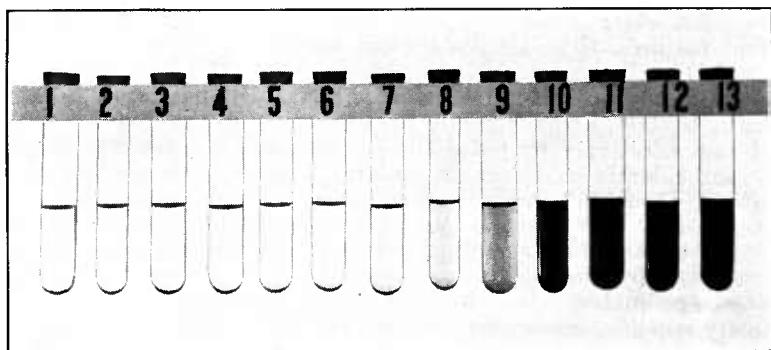


FIGURE 5.—Humus released from a soil in 0.2-normal solutions of sodium salts adjusted to pH 9.0. The anions added were: 1, Bromide; 2, aluminate; 3, thiosulfate; 4, chloride; 5, acetate; 6, nitrate; 7, sulfate; 8, water only; 9, phosphate; 10, carbonate; 11, silicate; 12, citrate; 13, oxalate. Before adding the above anions the soil was finely ground in 0.2-normal sodium tetraborate and washed twice with water.

important role in the fixation and release of boron by soils as well as by other materials. Methods other than those employed, nevertheless, are obviously essential, not only for adequate evaluation but also for satisfactory demonstration of anion exchange. The results obtained are not wholly unique in this regard, since no paper on anion exchange in soils has been found wherein stoichiometric replacement of one ion by another has been shown. In fact, there is a recurrent tendency toward passing over what might logically be regarded as the primary consideration. From the standpoint of an investigation of the subject of boron fixation, there did not appear to be immediate justification for pressing the matter further, the most effective of the anions tried being only slightly more effective than water alone.

If the same clarity characterized anion-exchange reactions as is often associated with cation-exchange reactions, it is self-evident that even exploratory work would have advanced an understanding of the phenomenon beyond that which now exists. The status of the existing

information cannot be ascribed wholly to analytical difficulties, even though they are admittedly greater than those involved in the determination of exchange-active bases such as calcium, magnesium, potassium, ammonium, and sodium. Some of the anion-forming elements have a high affinity for oxygen, giving rise to complex oxyacids. A number of these, if displaced from the exchange complex by a more active ion, would not remain in solution, and their displacement for that reason cannot be demonstrated at hydrogen-ion concentrations characteristic of soils. Furthermore, in the adsorption of oxyacids on the surface of minerals already containing much oxygen, it would be most natural to expect rearrangements of the structural linkages within the adsorbed radical, proceeding possibly to the loss of the original identity. The fixation or replacement by exchange of many anions accordingly can scarcely be expected to proceed along easily definable courses.

DISCUSSION OF THE FIXATION OF BORON BY SOILS

In view of the evidence of diversity in the behavior of boron between soils and probably between the fractions of boron in any one soil, and the absence of adequate information as to the nature of the radical or radicals in which boron is fixed, and the nature of the linkages involved, a discussion of this subject must unavoidably embrace many uncertainties. Some features of the data have nevertheless been regarded as sufficiently suggestive to warrant brief comment.

In the case of the drying of soil suspensions, whereby boron previously in solution in equilibrium with soil was fixed in such form that it did not return to solution on resuspension, it has seemed reasonable to believe that new compounds of low solubility resulted, possibly compounds with silica, which latter might, like silica gels, undergo an irreversible precipitation when desiccated. Otherwise no evidence has been developed by this work that boron fixation represents the formation of new boron compounds.

The boron in solution in soil suspension at pH 6 is probably in the form of boric acid, the dissociation constant of which is very low. At this pH value boron fixation may represent molecular adsorption. Frampton and Gortner (16) have concluded that the adsorption of weak electrolytes (organic acids) by charcoal is molecular rather than ionic, since the charge per unit area on the char particles is independent of the quantity of the acid adsorbed or in solution.

When boric acid is treated with sodium hydroxide, sodium tetraborate is formed, 0.1-normal solutions of which have a pH value of 9.2. Sodium tetraborate is dissociated to the extent of about 70 percent. The progressive increase in the fixation of boron with increasing pH values over the range from pH 6.0 to 9.0 may represent a progressive adsorption of B_4O_7 ions. If this adsorption is by an exchange reaction, then recognition must also be given to the fact that the concentrations of the anion OH is also increased, and these would therefore offer competition with the borate ions. With increasing pH values a progressive fixation of phosphate has also been found (8), but this increase in phosphate fixation was ascribed to precipitation.

The position of boron in the third periodic group and its amphoteric character, like aluminum, provides for the possibility that boron in

the form of a complex radical may be fixed by soil, or minerals, either as an acid or as a base. The small size of the boron atom would permit of its being surrounded by four closely packed oxygen atoms, as in the case of aluminum and silicon tetrahedra. The formation and fixation of such tetrahedra as additions or substitutions on the faces of soil materials, as during grinding when new surfaces with unsatisfied bonds are being opened, would undoubtedly result in tenaciously held boron.

The fact that boron fixed by a soil tends to be little dissociated and closely held even against high concentrations of other ions does not in any way preclude the possibility that its fixation represents a substitution for other anions. The results bearing most directly on this subject have only shown that once having been attached to newly opened surfaces this boron is not readily displaced.

SUMMARY

Evidence of a universal distribution of boron in soils is afforded by the fact that its compounds have always been found in natural waters and plant material when appropriate analytical methods have been employed. Boron deficiencies in soils have been reported from such widely separated places as New Zealand, Europe, British Columbia, and both the northwestern and eastern parts of the United States. Though the nature and source of soil-forming minerals is of principal importance, it appears that boron deficiency is most to be expected in regions of high rainfall. Boron injury is not uncommon in arid regions, and irrigation waters constitute the chief source of the excess boron.

Concentrations of boron in soil solutions of greatest agricultural concern can be roughly classified as belonging in one or the other of two categories: (1) Those concentrations that are insufficient to support normal plant growth, usually below 0.1 to 0.5 p. p. m., and (2) those concentrations that are so high as to cause injury, usually in excess of 0.5 to 5.0 p. p. m. Plant species and varieties show a wide variation in their boron requirements and in their boron tolerances. Between deficiency and injury a zone of concentration is normally to be expected wherein small changes have little effect upon growth. Irrigated soils were used for the investigations reported in this bulletin.

Upon addition of boron to soils a part of it is fixed by the soil and a part remains in the soil solution. Three mechanisms of fixation are considered—anion exchange, molecular adsorption, and chemical precipitation. The results of the investigation are such as to indicate that all three types of fixation may take place in soils, but it has not been possible to designate which one to the exclusion of the others is operative in any given case.

When boron was added to four test soils in amounts sufficient to produce initial soil-solution concentrations of 10 p. p. m., from 25 to 58 percent of it was fixed. At solution concentrations of 1,000 to 3,000 p. p. m. the order of the four soils was the same, but only 5 to 15 percent of the boron added was removed from solution. Equilibrium conditions between the soil and solution come about slowly. Upward to 15 percent more boron was fixed in a 300-day period than in a 30-day period.

High fixation capacity as measured in the laboratory was associated with a low degree of boron injury in the field.

If soils are suspended in boron solutions until equilibrium between the soil and solution is established, and then dried and resuspended, it is found that only a part of the boron previously in solution redissolves. Of four soils, drying had the greatest effect on the boron fixation by the two that had fixed least boron while in suspensions. A difference in the fixation reactions that take place in suspensions and those that accompany desiccation is indicated by these results.

Decreasing the pH value of 1-to-1 suspensions of four soils from 9 to 5.5 increased the concentration of boron in solution from twofold to fivefold. Below pH 5.5 the solubility of boron in two of the soils was further increased and in two of them it was decreased. The effect on boron solubility of increasing hydrogen-ion concentration in the soils by hydrochloric acid and carbon dioxide over the range 8 to 6 was found to be the same. The solubility of adsorbed boron is a function of the hydrogen-ion concentration or of a variable to which such concentration provides an index. Boron deficiency as induced by lining acid soils is discussed in this connection.

The solubility of soil boron in suspensions at boiling temperatures was three times as great as at a temperature of 21° C. On cooling in the presence of the soil, the initial solution concentration was re-established, indicating that previous heating had had no effect on the form in which the boron was held by the soil.

The boron fixed by continuously moist soils while being leached with solutions of boric acid was recovered when the leaching was continued with distilled water.

Comparisons of the quantity of boron brought into solution from 10 soils when wetted with a moisture-equivalent percentage of water, when repeatedly leached with cold water and with hot water, when extracted with acid and extracted with water after burning out the organic matter in the presence of sodium carbonate, point to a diversity in the forms in which boron was held by the different soils. The quantity of boron present in soil solutions was found to be only a small fraction of that released by the several methods of extraction.

Displaced soil solutions were studied, and they are regarded favorably as a means of measuring soil-solution concentrations. The use of 0.2-normal potassium sulfocyanate solutions as the displacing agent offers advantages over distilled water from the standpoint of rapidity of displacement and ease of testing (with ferric ammonium sulfate) for channeling in the displacement tubes.

Comparisons of the results obtained by soil-solution displacement with those obtained by extractions with 1.5 times the moisture-equivalent percentage of water appears to justify the latter method, which is more practical from the standpoint of a laboratory procedure. In using this method the soils are wetted for 2 days and then extracted with air pressure. The extractions can be made on a Buechner funnel if account is taken of evaporation loss in the suction flask. The 30 to 40 ml. of solution obtained from 500 to 1,000 gm. of irrigated soil is ordinarily sufficient for a boron determination. Wetting soils with larger quantities of water gave solution concentrations substantially lower than those found by displacement and by 1.5 moisture-equivalent extraction.

The boron found in the soil solutions of 38 irrigated lemon orchards of the San Fernando Valley was found to be correlated with boron in the leaves to the extent of $r=0.74\pm0.050$ in a series of samples collected in 1931. Samples from the same trees in 1936 gave $r=0.41\pm0.091$. The two years taken together as one array gave $r=0.59\pm0.050$. The soil samples uniformly represented the 6- to 36-inch horizon. A number of soil types were represented in the series.

As a consequence of boron fixation and the equilibrium between fixed boron and boron in solution, the soil solutions of the upper soil horizons are, to varying extents, found to be higher than those in the lower portions of the root zone, except where land had been irrigated with the same water supply for many years. The depth of root distribution varies greatly in different soils, and it was not expected that the soil samples taken to a uniform depth would satisfactorily evaluate diversity with respect to vertical distribution of boron and roots.

A correlation coefficient of -0.35 ± 0.78 was found between the moisture equivalent of the San Fernando soils, taken as an index of texture, and the boron in the soil solutions, taken as an inverse index to boron fixation.

An artificial zeolite was found to be several times more active as a boron-fixing agent than the soils worked with. Magnetite, which has an acid reaction, gave results in the same order as soils and of two bentonites; one fixed substantially more boron and one substantially less boron than the soils. A magnetite suspension at pH 8.9 fixed about twice as much boron as a suspension at pH 4.3.

A tourmaline-quartz mineral used as a substrate for the culture of plants released enough boron to cause severe injury. The effect is attributed to boron dissolved from the crystal matrices rather than from the tourmaline itself.

Grinding soil, kaolinite, and quartz sand in a ball mill resulted in a severalfold increase in boron fixation and in cation exchange capacity.

Anion exchange was studied by the following procedure: A soil was ground for 24 hours in a 0.2-normal sodium tetraborate 1-to-5 suspension, filtered, and washed twice with water. It retained 86 mg. of boron, or 23.8 mg.-equivalents of boron per 100 gm. On resuspension (1 to 20) in water and in a series of 0.2-normal sodium salts, boron (mg.-equivalent per 100 gm.) was displaced in the ascending order as follows: AlO_2 (3.1), CrO_4 , SiO_3 , acetate, water (4.35), Cl , S_2O_3 , CO_3 , NO_3 , Br , SO_4 , HPO_4 , citrate, and oxalate (5.6). Certain ions thus displace boron a little more effectively than water alone, but a low magnitude of displacement is represented in all cases. Much humate was displaced from the boron-treated soil by citrate and oxalate solutions, some by SiO_3 , CO_3 , and HPO_4 , and less by the remainder of the series than by water alone.

The use of soil amendments such as sulfur or lime for alleviating boron injury under field conditions where waters high in boron are in use can be expected to have opposite effects. Increasing soil acidity (or reducing alkalinity) by the addition of sulfur will increase the concentration of boron in the soil solution, and plant injury will be accentuated. When accompanied by an abundant use of water low in boron, sulfur may aid reclamation by increasing the concentration of boron in the subsoil percolate. Applications of lime will,

temporarily at least, decrease the hydrogen-ion concentration of many irrigated soils and thereby reduce the concentration of boron in the soil solution. Increasing the alkalinity of highly buffered soils above neutrality can be expected, however, to affect plant growth adversely because of nutritional disturbances. The use of either sulfur or lime on irrigated lands to change boron relationships cannot be encouraged except perhaps under exceptional conditions.

Biological analyses, preferably using as the test plant the particular crop in question, are regarded as being better suited to the study of the problem of boron deficiency of soils than chemical methods. The adequacy of the boron-supplying power of soils is as much a question of rate of release under the action of roots as of concentrations at static equilibrium between the soil and its solution.

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